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### CHEMICAL SCIENCES

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## CANADIAN JOURNAL OF RESEARCH

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# Canadian Journal of Research

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NUMBER 1

## THE ALKALOIDS OF *LYCOPODIUM* SPECIES

### X. *LYCOPODIUM CERNUUM* L.<sup>1</sup>

BY LÉO MARION AND R. H. F. MANSKE

#### Abstract

*Lycopodium cernuum* L., has yielded a new alkaloid, cernuine (L32),  $C_{16}H_{26}ON_2$ , nicotine, and an uncharacterized base (L33). Lycopodine could not be isolated.

Lycopodine has been found to be a constituent of all North American and European species of *Lycopodium* that have thus far been examined. However, it was not found in *Lycopodium saururus* collected in Argentina (1). This plant contained two new bases, saururine,  $C_{10}H_{19}N$ , and sauroxine,  $C_{17}H_{28}ON_2$ , for the latter of which, however, the present authors have suggested the formula  $C_{16}H_{24}ON_2$  (3). This suggestion receives some confirmation from the present work, since an alkaloid now found in *L. cernuum* L., for which the name cernuine is proposed, is best represented by  $C_{16}H_{26}ON_2$ . *L. cernuum* L. is native to the West Indian archipelago and was obtained in part from Hawaii through the kindness of Messrs. S. B. Penick and Co. of New York and in part from Trinidad where it was collected by Dr. E. M. Chenery, Department of Agriculture, Port of Spain, Trinidad, B.W.I., to whom we acknowledge our indebtedness. Lycopodine could not be isolated and its presence in amounts greater than 0.1 p.p.m. is very unlikely. Nicotine was present to the extent of about 0.1 p.p.m. Besides cernuine and nicotine the only other alkaloid (L33) isolated was obtained in such small amounts that an analysis of it was not possible. There remained small quantities of uncrystallized fractions that certainly contained other alkaloids. However, the total yield of crude alkaloids was only 0.01% and the chief constituent of this was cernuine.

#### Experimental

There was available 9100 gm. of dried *L. cernuum* L. from which the alkaloids were isolated by the procedure previously detailed (2). The crude alkaloid mixture was dissolved in cold aqueous oxalic acid and the filtered solution exhausted with ether (discarded). The solution was basified with ammonia and again exhausted with ether. The residue from this extract weighed 1.0 gm. It was subjected to slow distillation from a bulb heated in an air bath,

<sup>1</sup> Manuscript received August 5, 1947.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada, and the Research Laboratory, Dominion Rubber Co. Ltd., Guelph, Ont. Issued as N.R.C. No. 1660. For Part IX of this series, see J. Am. Chem. Soc. 69: 2126, 1947.

and the following fractions were collected: I, b.p. up to 118° C. (3 mm.); II, b.p. 130° to 135° C. (2 mm.); III, b.p. 140° to 142° C. (1.5 mm.); IV, b.p. 150° to 155° C. (1.5 mm.); V, b.p. 169° to 171° C. (1.0 mm.); and VI, b.p. 195° to 205° C. (1.0 mm.).

#### *Nicotine*

Fraction I weighed rather less than 1 mgm. but it had a pronounced odor of nicotine. It was converted into the dipicrate, which, when recrystallized from methanol, melted at 225° C.\* In admixture with an authentic sample of nicotine dipicrate it melted at 225° to 226° C.

#### *Cernuine (L 32)*

Fraction V slowly crystallized in the receiver as it distilled. It was recrystallized from ether-hexane, and it then melted at 106° C. This melting point remained constant when the base was recrystallized from a large volume of boiling hexane, in which it is only sparingly soluble. Cernuine thus obtained consisted of stout hexagonal prisms. Found: C, 73.36, 73.37; H, 9.95, 9.83; N, 10.47%. Calc. for  $C_{16}H_{26}ON_2$ : C, 73.28; H, 9.92; N, 10.69%. Including a small amount of perchlorate obtained from fraction IV and some recovered as perchlorate from the mother liquors, there was obtained about 0.2 gm. of cernuine.

The perchlorate of cernuine is excessively soluble in methanol or in acetone and could not be crystallized from either of these solvents in combination with ether or ethyl acetate. However, it crystallized readily from warm water in large plates that melted at 110° C. As thus obtained it is best represented as a sesquihydrate, which, when heated at 100° C. (1 mm.), lost 4.84% water, forming a brittle glass-like residue. The loss of 1  $H_2O$  from  $C_{16}H_{26}ON_2 \cdot HClO_4 \cdot 1.5 H_2O$  requires 4.62%. The analyses were carried out on the dehydrated material. Found: C, 51.62, 51.82; H, 7.18, 7.35; N, 7.46%. Calc. for  $C_{16}H_{26}ON_2 \cdot HClO_4 \cdot 0.5 H_2O$ : C, 51.68; H, 7.54; N, 7.54%.

#### *Alkaloid L33*

Fraction VI slowly deposited a small crop of crystals from its concentrated solution in ether. The base was recrystallized from boiling ether in which it is only sparingly soluble, and it then consisted of short stout prisms melting at 218° C. Insufficient material was obtained to permit an analysis.

Attempts to isolate crystalline material from fractions II or III or from the residue from the distillation were met with failure.

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\* All melting points are corrected.

## THE REACTION OF HYDROGEN ATOMS WITH BUTADIENE<sup>1</sup>

BY W. HAROLD WHITE<sup>2</sup> AND C. A. WINKLER

### Abstract

An investigation of the reaction of hydrogen atoms with butadiene was made at 28° and 252° C. by the Wood-Bonhoeffer method. Ethane was the main product, with butane, butene, propane, and methane occurring in smaller concentrations. Trace amounts of propylene and acetylene were also found. Temperature had little effect on either the nature or the relative proportions of the products. A possible mechanism for the reaction is outlined.

### Introduction

The conventional reactions of butadiene with a wide variety of compounds, such as the halogens and maleic anhydride, have been the subject of numerous studies. However, relatively little is known of the elementary reactions of this important alkadiene and its behavior in comparison with that of mono-unsaturated and saturated aliphatic hydrocarbons. The mercury photo-sensitized reaction of hydrogen and butadiene has been studied by Gunning and Steacie (4). The present paper describes an investigation of this reaction by the Wood-Bonhoeffer method.

### Materials and Procedure

The apparatus and experimental procedures were essentially the same as described previously (7, 11). In brief, commercial hydrogen, purified by passage over platinized asbestos at 500° C. and subsequently moistened, was partially decomposed in a Wood's discharge tube. The resulting hydrogen atoms were reacted with butadiene of greater than 98% purity in a Pyrex vessel maintained at either 28° or 252° C. Ethane and higher boiling products formed in the reaction were collected in a trap maintained at -180° C. Methane and some hydrogen were retained in a trap containing activated silica gel at -180° C.

A partial analysis of the products was obtained by low temperature Podbielniak distillation. Methane was determined by a combustion method (8), and acetylene and propylene in a Burrell gas analysis apparatus. The total C<sub>4</sub> fraction was treated with maleic anhydride to remove unreacted butadiene by a modification of a procedure described previously (10), and the resulting butene-butane mixture analyzed in the Burrell apparatus.

### Results

The experimental data obtained are given in Tables I and II. Approximately 34% of the butadiene reacted to form mainly ethane, with smaller

<sup>1</sup> Manuscript received June 5, 1947.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que.

<sup>2</sup> Holder of a Fellowship under the National Research Council of Canada; at present, Research Chemist, Imperial Oil Ltd., Sarnia, Ontario.

TABLE I  
EXPERIMENTAL CONDITIONS AND PRODUCTS FORMED IN THE REACTION  
OF BUTADIENE WITH HYDROGEN ATOMS

Run No.	Temp., ° C.	Press., mm.	Atom conc., %	Flow, moles/ sec. $\times 10^6$		Products, mole %										Buta- diene reacted %
						H <sub>2</sub>	C <sub>4</sub> H <sub>6</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>6</sub>	C <sub>4</sub> H <sub>8</sub>	
1	28	0.29	19.7	1.62	0.435	7.4	Trace	16.1		5.2		56.5	7.0	7.8	33.6	
2	29	0.29	19.7	1.62	0.433	7.0	Trace	16.2	0.9	3.7	58.8	6.5	6.9		31.3	
3	28	0.29	19.7	1.62	0.439	7.0	Trace	17.3	0.9	4.7	54.7	7.0	8.4		35.4	
4	253	0.30	13.9	1.62	0.433	5.8		14.7		11.2	54.9	6.3	7.1		35.8	
5	251	0.29	13.9	1.62	0.424	7.1		14.2	1.0	7.6	56.9	6.1	7.1		33.5	
6	251	0.30	13.9	1.62	0.441	6.4	1.4	11.3	1.5	7.8	57.4	6.4	7.8		33.7	

TABLE II  
PERCENTAGE CONVERSION OF BUTADIENE TO THE VARIOUS REACTION PRODUCTS

Run No.	% Conversion of butadiene to:						
	CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>4</sub>	C <sub>4</sub> H <sub>10</sub>
1	5.7	Trace	12.5		4.0	5.4	6.0
2	5.3	Trace	12.3	0.7	2.8	4.9	5.3
3	5.5	Trace	13.5	0.7	3.7	5.5	6.5
4	4.6		11.7		8.9	5.0	5.6
5	5.5		11.1	0.8	5.9	4.7	5.5
6	5.0	1.1	8.9	1.2	6.2	5.1	6.2

amounts of methane, propane, butane, and butene. Traces of acetylene and propylene were also present. Temperature had no marked effect on either the relative proportions of the products or on the total percentage conversion of butadiene. However, an increase in temperature was associated with some increase in the formation of propane and comparable decrease in that of ethane.

Calculations of the collision numbers, yields, and activation energies are given in Table III. In these, values of  $2.14 \times 10^{-8}$  cm. and  $4.37 \times 10^{-8}$  were taken as the diameters of the hydrogen atom (2) and butadiene molecule (9), respectively, and the steric factor assumed to be 0.1.

For reasons outlined in an earlier paper on the reaction of hydrogen atoms with propylene (5), no significance can be ascribed to the increase in observed activation energy with increased temperature, nor can the lower value of 7.5 kcal. be taken as the activation energy of the primary step. The high percentage conversion and temperature independence of the reaction suggest that the activation energy of the butadiene reaction, like that for the reaction of hydrogen atoms with ethylene (1, 3, 6), is probably of the order of 5 kcal. or less.

TABLE III

DATA FOR COLLISION YIELDS AND ACTIVATION ENERGIES IN THE REACTION OF BUTADIENE WITH HYDROGEN ATOMS

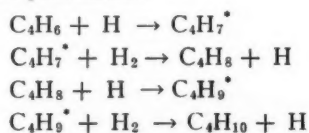
Run No.	Temp., °C.	Total flow corrected for hydrogen atoms, moles/sec. $\times 10^3$	Reaction time, sec.	Partial press. of hydrogen atoms, mm.	$Z_{C_4H_6 \cdot H}$ per sec. $\times 10^{-3}$	$Z_{C_4H_6 \cdot H}$ in reaction time $\times 10^{-3}$	Butadiene reacted, %	Collision yield $\times 10^7$	E, kcal., assuming $A = 0.1$
1	28	2.37	0.58	0.057	15.6	9.10	33.6	3.69	7.5
2	29	2.37	0.58	0.057	15.6	9.06	31.3	3.46	7.5
3	28	2.38	0.58	0.057	15.6	9.07	35.4	3.90	7.5
4	253	2.28	0.36	0.042	8.64	3.10	35.8	11.6	11.9
5	251	2.27	0.35	0.041	8.42	2.95	35.5	11.4	11.9
6	251	2.29	0.36	0.042	8.65	3.11	33.7	11.0	11.9

### Discussion

The main points to be considered in attempting to formulate a suitable mechanism for the reaction of hydrogen atoms with butadiene are: (a) the high percentage conversion of butadiene and relative temperature independence of the reaction as compared with paraffin hydrocarbons, and (b) insufficient hydrogen atoms were available from the discharge to effect the extensive decomposition and hydrogenation required in the formation of the predominantly saturated reaction products.

The results of the present study are quite comparable, at least qualitatively, with those obtained in the earlier study of the reaction of hydrogen atoms with propylene (5). For reasons similar to those outlined for the propylene reaction, the most probable primary reaction with butadiene should be hydrogenation, rather than abstraction of a hydrogen atom or a chain-splitting reaction. Similarly, further hydrogenation might be expected to follow the primary step, to form eventually the butyl radical. However, the extensive hydrogenation required for the observed butadiene conversion would almost entirely exhaust the hydrogen atoms available from the discharge, and there remains the problem of accounting for the formation of lower hydrocarbons, presumably by 'atomic cracking' reactions such as those proposed in similar studies with butane and isobutane (7, 11).

A similar scarcity of hydrogen atoms was noted in the study with propylene (5) and it was suggested that the results could be explained if it were assumed that hydrogenation yielded active propyl radicals which could react with hydrogen molecules at room and higher temperatures to form the saturated hydrocarbon and regenerate a hydrogen atom. With butadiene the following typical reactions might be postulated:





The maintenance of the hydrogen atom concentration in this way would permit the observed extent of butadiene conversion together with relatively large production of lower hydrocarbons by 'atomic cracking'. Furthermore, if the reaction of active radicals with hydrogen molecules is assumed to occur at lower, as well as higher, temperatures, the effective hydrogen atom concentration should be relatively independent of temperature. The nature and relative proportions of the products might then be expected, as they are in fact found, to be practically independent of temperature.

The observed increase in propane and decrease in methane and ethane contents of the products with increased temperature may be attributed to decreased reaction time, hence less 'atomic cracking' at the higher temperature.

Some decomposition of the energy-rich radicals might have occurred. Such reactions would generally yield unsaturated products, which could be saturated, presumably, only if the hydrogen atom concentration is maintained by reaction of the radicals with hydrogen molecules. Since the products of the over-all reaction were predominantly saturated, the extent of radical decomposition must have been comparatively small. Disproportionation and recombination of the radicals probably were also of little significance.

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# SOME NEW INDICATORS DERIVED FROM VANILLIN: 4-HYDROXY-3-METHOXY- $\beta$ -NITROSTYRENE AND HOMOLOGUES<sup>1</sup>

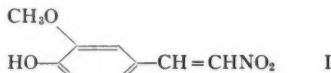
BY ROSS STEWART AND R. H. CLARK

## Abstract

Vanillin has been condensed with certain nitroparaffins to produce four compounds with indicator properties. The benzoyl derivatives of two of these were also synthesized. The color change, pH range, and indicator constant were measured for each of the four indicators.

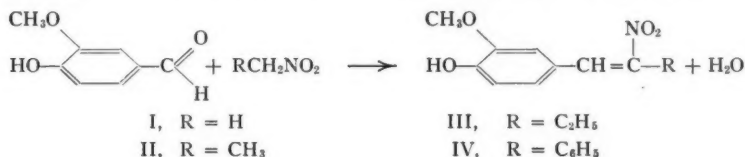
## Introduction

In 1904, Knoevenagel and Walter (3) synthesized the compound 4-hydroxy-3-methoxy- $\beta$ -nitrostyrene (I) and observed its intense red color in basic solution.



The compound was recommended as an indicator in 1925 by Rao and coworkers (6), who observed the color at several pH values. However, they did little quantitative work on its indicator properties. Since this compound showed interesting possibilities as an acid-base indicator it was decided to investigate its properties more thoroughly and to synthesize several of its homologues to determine their indicator properties, if any.

This compound and its homologues were synthesized after the method of Knoevenagel by condensing vanillin with the appropriate nitroparaffin.



Of the remaining three compounds II has been reported by Bruckner and Kramli (1) and more recently by Kulka and Hibbert (5); the latter's synthesis was similar to that reported here. The last member of the series, 4-hydroxy-3-methoxy- $\alpha'$ -nitrostilbene (IV), prepared from vanillin and phenylnitromethane, gave difficulty in that it would not crystallize from the reaction mixture as did the lower members of the series. Even on being frozen out with dry ice and alcohol and collected on a chilled funnel the typical yellow crystals, on being allowed to return to room temperature, melted before reaching 0° C. However, on refluxing with dilute hydrochloric acid followed

<sup>1</sup> Manuscript received August 12, 1947.

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C.

by cooling, crystals melting at 125° C. were obtained. This suggested the existence of two isomers, the high melting product being probably the stable *trans*-isomer and the low melting fraction probably a mixture of *cis*- and *trans*-isomers. No evidence of two isomers was found in any of our work on the other compounds.

The 4-benzoyl derivatives of II and III were prepared. They exhibit no indicator properties. An attempt to prepare both the 4-benzoyl- and 4-(4-nitrobenzoyl)-derivatives of the nitrostilbene led only to thick uncrystallizable oils.

### Experimental

All melting points reported were obtained with the Fisher hot stage melting point apparatus.

#### 4-Hydroxy-3-methoxy- $\beta$ -nitrostyrene (I)

Vanillin (15.2 gm., 0.1 mole) was dissolved in nitromethane (12.2 gm., 0.2 mole) and the minimum amount of absolute methanol to effect complete solution. Methylamine hydrochloride (0.5 gm.) and sodium carbonate (0.5 gm.) were mixed and added. The solution was allowed to stand in the cold overnight. On filtration and washing with a few milliliters of very dilute hydrochloric acid, 16.5 gm. of crystalline product was obtained. Recrystallization from hot alcohol yielded 14.4 gm. pure product (74%), melting at 169° C. (The literature melting points for this compound vary from 160° to 164° C. (7) to 167° C. (4).)

#### 1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-propene (II)

Vanillin (0.1 mole) was condensed with nitroethane (15.0 gm., 0.2 mole) in the manner above described. After the product had stood for three days 2 ml. of dilute hydrochloric acid was added and crystallization occurred to the extent of 15 gm. The mother liquor, on standing several more days at 0° C., yielded 5 gm. Two recrystallizations from hot alcohol gave 15 gm. of pure product (72%) melting at 103° C. (Literature melting points: 100° C. (1), 101° to 102° C. (5).)

#### 1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-butene (III)

Vanillin (0.1 mole) and 1-nitropropane (17.8 gm., 0.2 mole) were allowed to react as before. After the product had stood for seven days 2 ml. of dilute hydrochloric acid was added and 10 gm. of crystals was obtained. The mother liquor, on standing several days at 0° C., gave 3.5 gm. Recrystallization from hot alcohol yielded 12 gm. of bright yellow, flat rods (54%), m.p. 80.5° C. Further crystallizations did not alter the melting point. This compound is insoluble in acid, soluble in base, alcohol, and acetone. Calc. for  $C_{11}H_{13}O_4N$ : N, 6.28%. Found: N, 6.34, 6.36%.

#### 4-Hydroxy-3-methoxy- $\alpha'$ -nitrostilbene (IV)

Vanillin (4.0 gm.), phenylnitromethane (4.5 gm.), and 5 ml. of absolute methanol were mixed with methylamine hydrochloride (0.2 gm.) and sodium

carbonate (0.2 gm.) and allowed to stand overnight. Next day the dark, syrupy mass was refluxed for 15 min. with 3 ml. of dilute hydrochloric acid and set away at 0° C. The mass crystallized in from one to three days, yielding 1.1 gm. of fine yellow needles. The mother liquor, kept at 0° C. for seven days, yielded 1.6 gm. After recrystallization from hot alcohol a total of 1.7 gm. of fine bright yellow crystals was obtained, m.p. 124.8° to 125.5° C. (24%). A further crystallization did not change the melting point. This compound has solubilities similar to those of III. Calc. for  $C_{15}H_{13}O_4N$ : N, 5.17%. Found: N, 5.16, 5.17%.

*1-(4-Benzoyloxy-3-methoxyphenyl)-2-nitro-1-propene*

1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-propene (3.0 gm.) was dissolved in 3 ml. of pyridine, and benzoyl chloride (1.4 gm.) was added and the mixture stirred. Ten milliliters of water was added and the precipitate filtered out and washed with cold, dilute sodium carbonate solution until only a trace of pink coloration remained. The precipitate was then dissolved in hot alcohol from which it crystallized in fine light yellow plates that were insoluble in water but moderately soluble in alcohol and soluble in acetone. Yield 3.2 gm. (72%). Further crystallizations gave a constant melting point of 114.5° to 115.2° C. Calc. for  $C_{17}H_{15}O_5N$ : N, 4.47%. Found: N, 4.45, 4.48%.

This compound was also prepared in good yield by condensing vanillin benzoate with nitroethane.

*1-(4-Benzoyloxy-3-methoxyphenyl)-2-nitro-1-butene*

1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-butene (3.0 gm.) was treated exactly as in the previous procedure. Yield of light yellow crystals, melting at 86° C., was 3 gm. (68%). This compound has similar solubilities to the nitropropene derivative. Calc. for  $C_{18}H_{17}O_5N$ : N, 4.27%. Found: N, 4.24, 4.25%.

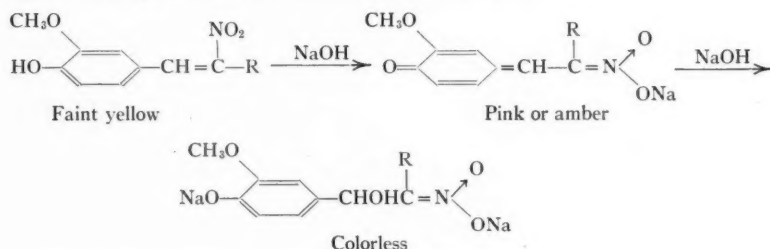
### Discussion

The color change of these indicators in extremely dilute solutions (2 : 1,000,000) is from faint yellow to pink for compounds I and IV and from faint yellow to amber for compounds II and III, going from acid to basic solution. All four fade to colorless in strongly basic solution but the sluggishness of this second color change renders it almost useless. In 1 *N* sodium hydroxide the color of I fades to colorless within 30 sec., but the color of III takes up to five minutes to disappear entirely. In 0.1 *N* sodium hydroxide the rate of fading is much less although a colorless solution is again the ultimate result. The time that the colors of these indicators take to drop to half their original color intensity in 0.1 *N* sodium hydroxide is given in Table I. These values were measured approximately by means of a Klett photoelectric colorimeter using 2 drops of 0.1% indicator solution per 5 ml. of 0.1 *N* sodium hydroxide.

TABLE I  
INDICATOR PROPERTIES

Name	pH range and color change		$pK_I$	Rate of fading in 0.1 N NaOH, $t_{1/2}$ minutes
4-Hydroxy-3-methoxy- $\beta$ -nitrostyrene	6.1 Faint yellow	8.1 Pink	7.6	1.3
1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-propene	6.8 Faint yellow	8.8 Amber	8.2	7.2
1-(4-Hydroxy-3-methoxyphenyl)-2-nitro-1-butene	6.8 Faint yellow	8.7 Amber	8.1	11.8
4-Hydroxy-3-methoxy- $\alpha'$ -nitrostilbene	6.4 Faint yellow	8.4 Pink	7.7	5.2

Hahn and Stiehl's (2) theory of the color change mechanism of the hydroxy-nitrostyrenes is applicable to all members of this series.



The pH range of each of these indicators is about 2 pH units. Although the limits of the color change are not sharp the color change itself is very distinct. The ranges were measured using small Nessler tubes and 0.06 *M* buffers of known pH. The indicator constants,  $pK_I$ , were estimated by means of the Klett colorimeter.

The indicators were made up in 0.1% alcoholic solution and apparently remain stable indefinitely. From 5 to 8 drops of these solutions per 100 ml. is required for ordinary colorimetric work.

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## COPPER (II) AND NICKEL (II) CO-ORDINATION COMPOUNDS WITH DIETHYLENETRIAMINE AND HYDROXY- ETHYLETHYLENEDIAMINE<sup>1</sup>

BY J. G. BRECKENRIDGE

### Abstract

The reactions of diethylenetriamine and hydroxyethylethylenediamine with copper (II) and nickel (II) chloride and bromide have been shown to give a variety of stable, highly crystalline products. With diethylenetriamine (dn), the two metals behaved in a parallel manner, either one or two 'dn' molecules co-ordinating to the metal, thus confirming the deductions of others from spectrophotometric work. With hydroxyethylethylenediamine (hn), either one or two 'hn' molecules co-ordinated with copper, and three with nickel.

### Introduction

The complex compounds formed by co-ordination of polyfunctional (multidentate) organic amines with metals are of interest from many points of view, particularly with respect to the geometry of the molecule or ion formed and the co-ordination number of the central metal atom or ion. In many cases the ease of formation, the stability, and the depth of color of these substances has led to their use in analytical procedures. The present paper describes the compounds formed by reaction between copper (II) and nickel (II) chlorides and bromides and two organic bases, diethylenetriamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ ) and hydroxyethylethylenediamine ( $\text{HOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ ).

### Part I. Diethylenetriamine (dn) Compounds

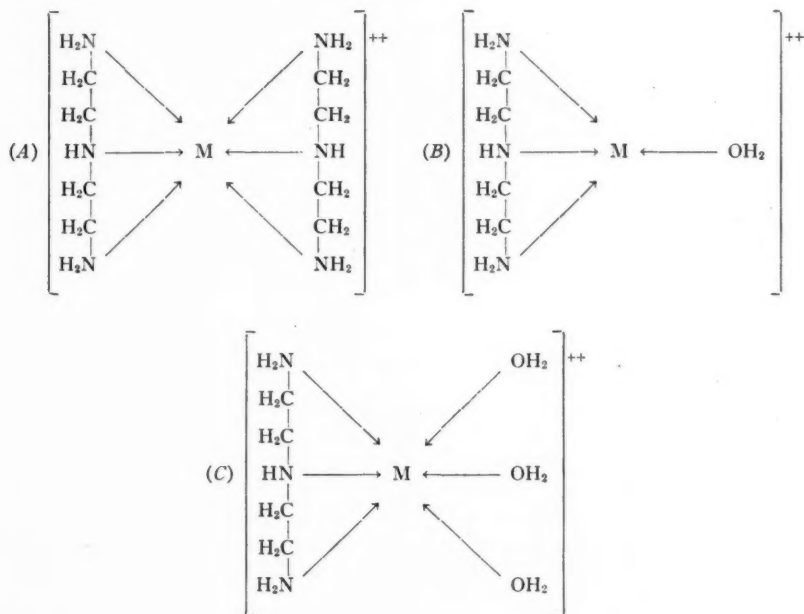
Co-ordination compounds of this base with metals were described first by Mann (6), who isolated compounds with platinum, rhodium, cobalt, and copper. Copper (II) thiocyanate gave a product of formula  $[\text{Cu dn SCN}]\text{SCN}$ , the copper being 4-co-ordinated, while copper (II) iodide gave a product to which the formula  $[\text{Cu}_2 \text{dn}_3 \text{I}_4]$  was attributed, the compound being non-ionic, and the metal atoms with co-ordination numbers of 6. The latter compound on treatment with carbon dioxide broke up and produced a compound analogous to the thiocyanate.

From the above work, Mann drew the conclusion, reinforced by observations on platinum (II) compounds, that the normal product of reaction between a potentially tridentate base and a 4-co-ordination metallic atom will be that in which all three functional groups of the base are co-ordinated. In other words, a compound such as  $[\text{Cu dn}_2]\text{X}_2$  would be unlikely to exist with the copper in the 4-co-ordinated state.

<sup>1</sup> Manuscript received August 1, 1947.

Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont.

A spectrophotometric study of solutions of copper (II) salts and varying amounts of the base was carried out by Job and Brigando (3), who reported that preliminary results suggested the existence of the  $[\text{Cu}_3 \text{dn}_4]^{++}$  ion in solution. This work was repeated and extended by Haendler (2), who investigated the complex ions of the base with copper (II) and nickel (II). Haendler concluded that the ions  $[\text{Cu dn}]^{++}$ ,  $[\text{Cu dn}_2]^{++}$ ,  $[\text{Ni dn}]^{++}$ , and  $[\text{Ni dn}_2]^{++}$  existed in aqueous solution, that there was no evidence for the existence of the ion suggested by Job and Brigando, and that in each case the base was functioning as a tridentate molecule. If the latter assumption is correct, the ions having a metal:base ratio of 1:2 must have the metal in the 6-co-ordinated state, which is normal for nickel but not usual for copper, and the structure of the ion would be (A). In the case of the ions with a metal:base ratio of 1:1, the metal could be either 4-co-ordinated as in (B), or 6-co-ordinated as in (C).



The complex compounds of the base described in this paper are all highly water soluble, and their isolation from aqueous solution proved to be difficult, but when 95% ethanol was used as the reaction medium, crystalline products were readily formed. The general procedure was to mix varying amounts of the base in 95% ethanol with known amounts of the copper (II) or nickel (II) chloride or bromide in 95% ethanol. The reactions were strongly exothermic, sufficiently so as to boil the solvent if concentrated solutions were used. The crystalline products isolated and characterized are described below.

## COMPOUNDS WITH METAL:BASE RATIO OF 1:2

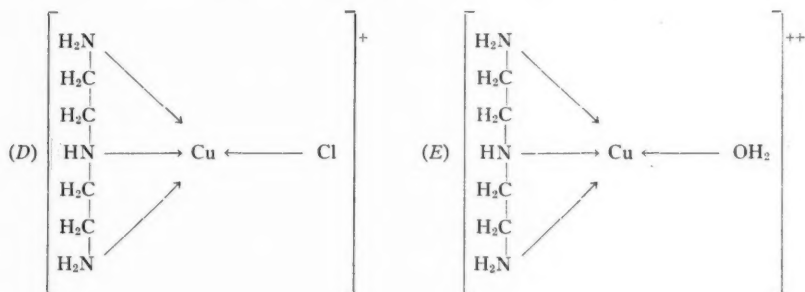
These were formed when the reactants were mixed in the correct proportion or if excess base was used, there being no evidence of any compound containing more than two moles base per mole metal halide. With the copper halides, mixture of the reactants produced the characteristic very deep blue solution, from which the product crystallized within a few minutes. The dark purple-blue crystals could be easily recrystallized from 95% ethanol. The reaction with the nickel halides was similar, the initial mixture of the reactants being deep purple, the product crystallizing rapidly, and recrystallization being easy. Analysis of the four products gave the general formula  $M dn_2 X_2 \cdot H_2O$ . The position of the molecule of water is somewhat uncertain; it is not usual for compounds of this type to contain water of hydration, but some cases are known. The water was bound very firmly, and prolonged heating (10 hr. or more) *in vacuo* over phosphorus pentoxide at 100° C. was necessary to remove it. No reasonable formula could be deduced in which the water is co-ordinated, and since freezing point and conductivity measurements on dilute aqueous solutions of the compounds pointed to the existence of three gram-ions in solution per formula weight, the water molecule is presumably water of hydration which is an essential part of the three dimensional structure of the crystal. When the reaction between copper (II) chloride and the base was carried out under anhydrous conditions, a product was formed of formula  $Cu dn_2 Cl_2$ , which was very hygroscopic. Exposure to air for a few minutes transformed it to the monohydrate.

The same general formula applies to both the copper and nickel complexes, and in view of the occurrence of the one water molecule in both, it seems reasonable to conclude that the structure of the ions is similar, thus corroborating the suggestion of Haendler (2). Since the nickel is almost certainly 6-co-ordinated, the copper is presumably in the same state, and the structure of the ions will be as in (A), the arrangement around the central atom being octahedral. There should be three possible geometrical isomers of this structure, as pointed out in another case by Mann and Pope (7), but only one product was isolated from each reaction in the present work. The other possibility is that the base is only functioning as a bidentate molecule with the copper, the latter being 4-co-ordinated, but this seems less likely. X-ray powder photographs of the copper and nickel chloride complexes, taken through the courtesy of Dr. M. A. Peacock of the Department of Geological Sciences, showed some similarity, but not sufficient to adduce this as evidence. It is hoped to have a complete crystallographic examination carried out in the near future.

When the copper halide compounds were treated with hydrochloric acid, yellow crystalline products were formed, apparently the chlorocuproate compounds described by Jonassen, Crumpler, and O'Brien (4), which were not investigated further.

## COMPOUNDS WITH METAL:BASE RATIO OF 1:1

When equimolar amounts of copper (II) chloride and the base were used, a dark blue crystalline material was produced, markedly different in appearance from the 1 : 2 ratio product. Analysis gave the formula  $\text{Cu dn Cl}_2$ , the structure of which is probably as shown in (D), comparable to the iodide and thiocyanate isolated by Mann (6). A hydrated form was obtained from aqueous solution, analysis agreeing with a hemihydrate. Since freezing point measurements on dilute aqueous solutions checked with the presence of three gram-ions per formula weight, the structure in aqueous solution is probably as in (E), a water molecule displacing the co-ordinated chlorine.



With nickel (II) chloride, use of a slight excess of base over that required for equimolar proportions resulted in a deep indigo-blue solution, from which a mixture of purple and greenish-blue crystals separated. The purple crystals were identical with those described before (the 1 : 2 compound), while the greenish-blue product analyzed for a compound of formula  $\text{Ni dn Cl}_2 \cdot \text{H}_2\text{O}$ . The latter could also be obtained in the anhydrous state as green crystals, and in a higher state of hydration (apparently a tetrahydrate) as indigo-blue crystals. The complex ion in solutions of this 1 : 1 compound might be either (B) or (C), but it has been shown by Werner (8) that in some cases solutions with 4-co-ordinated nickel ions are blue, and those with 6-co-ordinated nickel, purple. In the present work it was found that titration of an aqueous solution of the purple 1 : 2 compound with dilute acid produced a color change to blue when two equivalents of acid had been added. The ion in solution at this point almost certainly has the two acid molecules combined with one of the primary amino groups of each of the two molecules of the base, leaving the nickel 4-co-ordinated.

It is probable, therefore, that aqueous solutions of the 1 : 1 copper and nickel complexes contain the ion as shown in (B), the metal being 4-co-ordinated. In the crystalline state the 1 : 1 nickel complex is probably analogous to (D).

## EXPERIMENTAL

Diethylenetriamine was purified by distillation *in vacuo* in an all-glass apparatus, the product coming over at 93° to 94° C. at 17 mm. pressure. The copper and nickel halides were reagent grade. The melting points of the products recorded below are uncorrected; decomposition was evident in most cases, and the melting points varied somewhat according to the rate of heating.

[Cu dn<sub>2</sub>] Cl<sub>2</sub> · H<sub>2</sub>O.—Seventeen grams (0.1 mole) cupric chloride dihydrate in 200 ml. 95% ethanol was added to 21 gm. (0.2 mole) base in 50 ml. 95% ethanol. From the resulting dark purple-blue solution crystals rapidly separated on cooling, in nearly theoretical yield. The material was recrystallized twice from 95% ethanol, the final product being in the form of hard, well formed, clear, dark purple-blue crystals, melting at 197° C. The same product was obtained when the proportion of base was increased up to a great excess. Freezing point measurements on dilute aqueous solutions gave an apparent molecular weight = 119 (calc. = 120, assuming three gram-ions per formula weight). Dehydration over phosphorus pentoxide *in vacuo* at 100° C. for at least 10 hr. removed the water of crystallization. Addition of concentrated hydrochloric acid to an aqueous solution gave a golden-yellow crystalline product, decomposing at 210° C. A solution of this, on addition of dilute alkali, turned the deep blue color characteristic of the original complex.

[Cu dn<sub>2</sub>] Cl<sub>2</sub>.—The anhydrous form of the previous compound was obtained by mixing anhydrous cupric chloride and the base in absolute ethanol. The product was a light blue microcrystalline powder, which on exposure to air rapidly gained weight and took on the purple-blue tint characteristic of the monohydrate.

[Cu dn<sub>2</sub>] Br<sub>2</sub> · H<sub>2</sub>O.—This was prepared in the same way as the chloride, the product being almost indistinguishable in appearance, and melting at 199° C.

[Cu dn Cl] Cl.—Seventeen grams (0.1 mole) cupric chloride dihydrate in 200 ml. 95% ethanol was added to 10 gm. (0.097 mole) base in 50 ml. 95% ethanol. Dark blue crystals separated on cooling; these were recrystallized from 95% ethanol, giving soft dark blue leaflets, melting at 205° C. These were stable in air, and showed no tendency to hydrate. Freezing point measurements on dilute aqueous solutions gave an apparent molecular weight = 78 (calc. = 79, assuming three gram-ions per formula weight).

[Cu dn Cl] Cl ·  $\frac{1}{2}$ H<sub>2</sub>O.—The hemihydrate of the previous compound was obtained by slow evaporation of a concentrated aqueous solution, the product appearing as hard, clear deep blue, monoclinic thick-tabular crystals. The water of hydration was easily removed over phosphorus pentoxide *in vacuo* at 100° C., the crystal structure breaking down to give a soft deep blue powder.

[Ni dn<sub>2</sub>] Cl<sub>2</sub> · H<sub>2</sub>O.—This was prepared as for the corresponding cupric chloride compound. The dark purple solution obtained after mixing the



reagents rapidly deposited brilliant purple crystals in nearly theoretical yield. These were recrystallized twice from 80% ethanol, the product being hard clear purple crystals, melting at 232° C. Excess of base over that required afforded the same product, and freezing point determinations checked for three gram-ions per formula weight (apparent molecular weight found = 113, calc. = 118). Intensive dehydration over phosphorus pentoxide was necessary to remove the water of hydration.

[Ni dn<sub>2</sub>] Br<sub>2</sub> · H<sub>2</sub>O.—This was prepared in a similar manner, yielding a product of the same appearance, melting at 248° C.

[Ni dn Cl] Cl · H<sub>2</sub>O.—Twenty-four grams (0.1 mole) nickel chloride hexahydrate in 200 ml. 95% ethanol was added to 12 gm. (0.12 mole) base in 50 ml. 95% ethanol. The deep indigo-blue solution on standing deposited a mixture of purple and greenish-blue crystals, which were separated by hand. The purple crystals were the 1 : 2 compound, while the green-blue product analyzed for the formula given. They could be recrystallized from 95% ethanol or from acetone-water. When brought in contact with water they underwent a color change to deep blue before dissolving, and evaporation of an aqueous solution gave a few deep blue crystals, insufficient for a complete

TABLE I  
ANALYTICAL RESULTS FOR 'dn' COMPOUNDS

Compound		Metal %	Halogen %	Nitrogen %	Water %
[Cu dn <sub>2</sub> ] Cl <sub>2</sub> · H <sub>2</sub> O	Calc.	17.7	19.8	23.4	5.0
	Found	17.7	19.8	23.1	5.1
[Cu dn <sub>2</sub> ] Cl <sub>2</sub>	Calc.	18.6	20.8	—	0
	Found	18.5	20.7	—	0
[Cu dn <sub>2</sub> ] Br <sub>2</sub> · H <sub>2</sub> O	Calc.	14.2	35.8	18.8	4.0
	Found	14.2	35.7	18.6	4.0
[Cu dn Cl] Cl	Calc.	26.8	29.8	—	0
	Found	26.8	29.8	—	0
[Cu dn Cl] Cl · $\frac{1}{2}$ H <sub>2</sub> O	Calc.	25.8	28.8	—	3.7
	Found	25.5	28.6	—	3.7
[Ni dn <sub>2</sub> ] Cl <sub>2</sub> · H <sub>2</sub> O	Calc.	16.6	20.1	23.7	5.1
	Found	16.6	20.1	23.7	5.0
[Ni dn <sub>2</sub> ] Br <sub>2</sub> · H <sub>2</sub> O	Calc.	13.3	36.1	19.0	4.1
	Found	13.1	36.1	18.6	3.8
[Ni dn Cl] Cl · H <sub>2</sub> O	Calc.	23.4	28.2	—	7.2
	Found	23.0	28.0	—	7.4
[Ni dn Cl] Cl	Calc.	—	30.4	—	0
	Found	—	30.2	—	0
[Ni dn Cl] Cl · 4H <sub>2</sub> O	Calc.	—	23.2	—	—
	Found	—	22.9	—	—

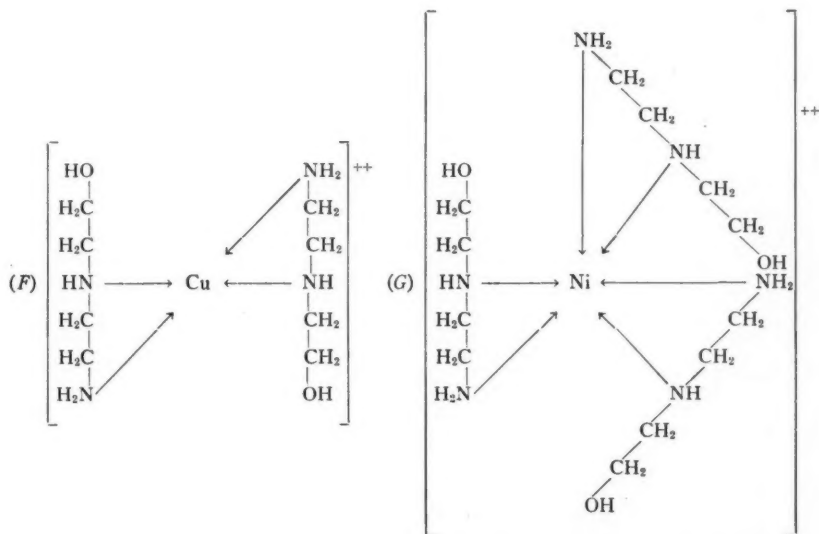
analysis. Analysis for halogen indicated only that the compound was the tetrahydrate. On dehydration of the green-blue monohydrate over phosphorus pentoxide, the water was readily removed, the crystals breaking down to a light green powder, which, on exposure to air, took up the molecule of water again. The anhydrous form could also be obtained by crystallization from a solution of the monohydrate in absolute ethanol, the product appearing as hard clear green crystals, which, on standing, slowly took on the blue tint of the monohydrate.

The analytical figures for the compounds described above are summarized in Table I, the 'found' values being averages of at least two concordant determinations, except in the case of the tetrahydrate of the 1 : 1 nickel compound.

### Part II. Hydroxyethylethylenediamine (hn) Compounds

This molecule contains a primary amino group, a secondary amino group, and a hydroxyl group, and might be expected to function normally as a bidentate molecule, the co-ordinating power of the oxygen being slight. The molecule is similar to 1,3-diaminopropanol-2, compounds of which with nickel have been described by Mann (5), and with copper by Breckenridge and Hodgins (1).

With copper (II) chloride and bromide, crystalline products were obtained, analysis agreeing with the formula  $\text{Cu hn}_2 \text{X}_2$ . These are comparable to the diaminopropanol compounds, and were almost indistinguishable in appearance. The structure of the ion may be represented as (F). A compound with copper chloride containing the metal and base in a 1 : 1 ratio was also obtained as a hemihydrate. In this case the oxygen is presumably also co-ordinated, the



fourth co-ordination position being taken by a chlorine in the solid state, and by a water molecule in solution, a situation similar to the corresponding 'dn' compound described in Part I.

With nickel (II) chloride, the only compound isolated from reaction mixtures containing widely varying proportions of reactants corresponded to the formula  $\text{Ni hn}_3 \text{Cl}_2$ . This was somewhat unexpected, since with diamino-propanol Mann (5) found that only two molecules of the base would co-ordinate, the nickel ion apparently having the planar 4-co-ordinated structure. In the present case the nickel is evidently 6-co-ordinated, and the ion may be represented as (G). In both (F) and (G) there are obvious possibilities of isomerism, but no evidence was found to demonstrate this.

#### EXPERIMENTAL

Hydroxyethylethylenediamine was purified by distillation *in vacuo* in an all-glass apparatus, the product coming over at 125° to 130° C. at 10 mm. pressure. The metal halides were reagent grade.

[Cu  $\text{hn}_2$ ]  $\text{Cl}_2$ .—This was prepared by mixing solutions of the metal salt and the base in 95% ethanol, using the correct molar proportions or excess amine. The reaction was exothermic, and from the dark blue solution a good yield of bright purple-blue crystals came down. These were recrystallized from 90% ethanol, the product melting at 194° C.

[Cu  $\text{hn}_2$ ]  $\text{Br}_2$ .—This was prepared in a similar manner. The product had the same appearance, and melted at 175° C.

[Cu  $\text{hn Cl}$ ]  $\text{Cl} \cdot \frac{1}{2} \text{H}_2\text{O}$ .—When the ratio of metal salt to base was 1:1, the resulting blue solution deposited bright blue needles, lacking the purple tint of the previous compounds. After recrystallization from 95% ethanol, the product melted at 148° C. The water of crystallization was readily removed over phosphorus pentoxide, the crystal structure breaking down to leave a blue powder.

TABLE II  
ANALYTICAL RESULTS FOR 'hn' COMPOUNDS

Compound		Metal %	Halogen %	Nitrogen %	Water %
[Cu $\text{hn}_2$ ] $\text{Cl}_2$	Calc.	18.6	20.7	16.3	0
	Found	18.7	20.7	16.3	0
[Cu $\text{hn}_2$ ] $\text{Br}_2$	Calc.	—	37.0	13.0	0
	Found	—	37.0	12.9	0
[Cu $\text{hn Cl}$ ] $\text{Cl} \cdot \frac{1}{2} \text{H}_2\text{O}$	Calc.	25.7	28.6	11.3	3.6
	Found	25.4	28.4	11.2	3.8
[Ni $\text{hn}_3$ ] $\text{Cl}_2$	Calc.	13.3	16.0	19.0	0
	Found	13.4	16.1	18.9	0

[Ni  $hn_3$ ]  $Cl_2$ .—This was prepared by mixing solutions of the metal salt and the base in absolute ethanol, using a 1:3 ratio. Small bright purple crystals were obtained, which, after recrystallization from 95% ethanol, melted at 172° C. The crystallization was much slower than with the copper compounds, and the crystals were not as well formed. No crystalline product other than this could be isolated from mixtures containing various proportions of the reactants, an excess of base over the 1:3 ratio giving the same compound, and an insufficiency of base not affording any identifiable product.

The analytical figures for the compounds described above are summarized in Table II, the 'found' values being averages of at least two concordant determinations.

#### Acknowledgment

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THE DENSITY OF ADSORBATES<sup>1</sup>BY N. G. M. TUCK,<sup>2</sup> R. L. McINTOSH, AND O. MAASS

## Abstract

The apparent density of the adsorbate and the adsorption isotherm have been measured in the systems carbon tetrachloride-charcoal and diethyl ether-charcoal. In both, the apparent density of the adsorbate is lower than the normal liquid density. These abnormally low values cannot be explained on the basis of the coexistence of 'vapor' and 'liquid' adsorbed phases. The results are consistent with the concept of the adsorbate's blocking-off a portion of the internal voids of the charcoal. The Langmuir equation represents the isotherm only when the quantity adsorbed exceeds two-thirds of the saturation value. The Harkins-Jura equation is valid at low relative pressures in the carbon tetrachloride-charcoal system, but not in the diethyl ether-charcoal system. Neon is adsorbed appreciably on charcoal at 25°C. and therefore cannot be employed to examine the effect that the gas being used for the measurements has on the apparent density of the adsorbate. Until more accurate data are available for the adsorption of helium on charcoal, both in the absence and presence of other adsorbates, the density of charcoal and the density of the adsorbate measured by helium displacement remain suspect. In view of the uncertainties, the utility of apparent density values of adsorbates in checking the concepts of the various theories of physical adsorption is limited.

## Introduction

A full understanding of the phenomenon of adsorption cannot be obtained from measurements of the adsorption isotherms and heats of adsorption alone. The various theories of adsorption are based mainly on such measurements but all include postulates concerning the nature of the adsorbed film. Recently, in attempts to check the validity of these postulates, measurements have been made of the changes that occur in certain physical properties of the adsorbate and the adsorbent during the process of adsorption. One of the properties that has been investigated is the so-called 'density' of the adsorbate.

If it is assumed that helium is not adsorbed, the free volume of a cell containing a porous solid can be computed from the pressure change resulting from the expansion of helium from a system of known volume into the adsorption cell. By repeating this procedure after a definite weight of adsorbate has been introduced into the adsorption cell, it is possible to determine the apparent volume, and thus the apparent density of the adsorbate. Among those who have used this technique of helium displacement are: Ewing and Spurway (4), who determined the density of water adsorbed on silica gel; Danforth and DeVries (3), who investigated the carbon tetrachloride-charcoal and acetone-charcoal systems; and Morrison and McIntosh (13) who measured the density of water adsorbed on charcoal.

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<sup>2</sup> Holder of a Studentship under the National Research Council of Canada. Present address: Pulp and Paper Research Institute of Canada, Montreal.



In interpreting the results, Ewing and Spurway (4), Danforth and DeVries (3), and Brunauer (1) have assumed that the apparent density of the adsorbent is not affected by the presence of the adsorbate. Density values of the adsorbate higher than that of the normal liquid are interpreted as indicating compression of the adsorbed molecules by surface forces, and lower density values as being due to the coexistence of vapor and condensed surface phases. Morrison and McIntosh (13) alternatively suggest that high values would be expected if the density being measured was that of individual molecules rather than that of a phase, while low values could be due to the adsorbate's blocking off some of the voids of the adsorbent.

The precise meaning of the terms 'vapor phase' and 'liquid phase' when applied to an adsorbate by the above authors (1, 3, 4) is not clear. Harkins and Jura (7, pp. 33-40) have defined four phases of films on solid sub-phases, namely: gaseous, liquid expanded, liquid intermediate, and condensed—in terms of equations of state. For the gas phase and condensed phase these equations are:

$$\pi\sigma = kT$$

and

$$\pi = b - a\sigma$$

respectively, where:

$\pi$  is the decrease in the surface free energy caused by the adsorption of a gas or vapor,

$\sigma$  is the surface area per adsorbed molecule,

$k$  is Boltzmann's constant,

$T$  is the absolute temperature,

$a$  and  $b$  are constants.

These can be transformed into the corresponding pressure - volume adsorbed relations:

$$V = KP$$

and

$$\ln P = B - A/V^2$$

by substituting in the Gibbs' adsorption equation.

Harkins, Jura, and coworkers (9-12) have also investigated phase transitions of films on solids. If a first order phase change occurs, such as the transition of a gaseous film to a liquid expanded, liquid intermediate, or condensed film, the equilibrium pressure of the adsorbate remains constant as the amount adsorbed varies. Consequently, if the low apparent density of the adsorbate is due to the coexistence of vapor and condensed phases of the Harkins-Jura type, then, over that region of the adsorption isotherm that corresponds to a region of low density of the adsorbate, the equilibrium pressure of the adsorbate should be constant.

According to Guest, McIntosh, and Stuart (5) the apparent density of charcoal measured by liquid displacement is lower than that obtained by helium displacement. This they interpreted as indicating the existence of internal voids that were accessible to helium but inaccessible to liquids. If a

liquid blocks off a certain proportion of the internal voids it is possible that the same liquid when used as an adsorbate would do likewise. If this does occur, then the change in the volume of an adsorbate-adsorbent system will consist of the volume of the adsorbate added plus the volume of the blocked-off voids.

In this investigation the system carbon tetrachloride - charcoal has been studied in some detail and preliminary results have been obtained for the diethyl ether - charcoal system. The results cannot be explained on the basis of the coexistence of gaseous and condensed phases of the Harkins-Jura type. The results indicate rather that the adsorbate blocks off a portion of the internal voids; the apparent density of the adsorbent is thus a function of the quantity of adsorbate present.

### Experimental

The charcoal was a zinc chloride activated material obtained from the National Carbon Company and designated as C.W.S.N. 178 B-2. A sample of this same charcoal was employed by Morrison and McIntosh (13). Approximately 35 gm. of charcoal was used.

The apparatus used for the greater portion of the experimental work was essentially the same as that described by Morrison and McIntosh (13) except for the following modifications:

(1) The liquid to be adsorbed was condensed from a storage bulb into a dilatometer calibrated to 0.001 cc.; the volume was measured at 0° C. and a correction added for the weight of vapor in adjoining lines. The liquid was then allowed to re-evaporate and was condensed into the expansion system; from there it was adsorbed on to the charcoal.

(2) During desorption runs the adsorbate was condensed from the cell of activated charcoal into bulbs that could be removed from the system and weighed.

(3) The stopcocks in the expansion-adsorption system were replaced by mercury cutoffs. These cutoffs were of two types, the porous disk valve which is described by Warrick and Fugassi (14) and check valves.

The procedure for determining the volume of the free space in the adsorption cell was the same as that described by Morrison and McIntosh (13) except that after apparent equilibrium had been established the amount of vapor carry-over from the expansion system into the adsorption cell was determined. The significance of the vapor carry-over will be discussed later. Briefly the steps were as follows:

(1) After the introduction of the appropriate quantity of adsorbate the equilibrium pressure of the system was measured.

(2) The cutoff between the expansion bulb and the charcoal bulb was closed; since this compressed the vapor in the expansion system slightly, the vapor pressure was again measured. Helium was admitted to the expansion system and the total pressure measured. The helium pressure was assumed to be the total pressure less the vapor pressure.

(3) The helium-vapor mixture was expanded into the adsorption cell and pressure-time readings taken until the pressure became constant. (Morrison and McIntosh (13) assumed that the final pressure of helium was equal to the final total pressure less the initial vapor pressure.)

(4) The cutoff to the adsorption cell was closed, the expansion bulb was immersed in liquid air for a period of one to three hours and the helium evacuated. This evacuation required from 10 to 15 min. The condensed vapor was allowed to re-evaporate and the vapor pressure measured. The final vapor pressure was computed from this measured pressure and the ratio of the two vapor pressures as measured in steps 1 and 2. The final helium pressure was assumed to be final total pressure as measured in step 3 less the final vapor pressure.

The volume of the free space in the adsorption cell was computed from the known volume of the expansion system and the initial and final helium pressures as measured in steps 2 and 4.

A second apparatus was built with which it was possible to obtain more accurate results when only small quantities of adsorbate were present. The expansion-adsorption system of this apparatus (Fig. 1) consisted essentially

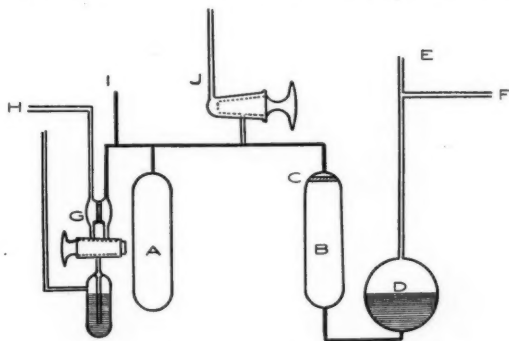


FIG. 1. The second apparatus used for measuring the density of the adsorbate.

of a cell containing activated charcoal, *A*, connected through a short length of capillary tubing to an expansion bulb, *B*. The expansion bulb, *B*, which contained a fritted glass disk, *C*, sealed inside near the top, was connected at the bottom by capillary tubing to a mercury reservoir, *D*. The volume between the capillary tubing and the porous disk was known. The mercury could be transferred to or from the expansion bulb at will by varying the pressure in the reservoir, using a three way stopcock at *E*. This stopcock could be opened to the vacuum line or to the atmosphere as desired. Fine adjustments were made with a Toepler pump at *F*.

To determine the volume of the free space in the adsorption cell, *A*, helium was expanded from the adsorption cell into the expansion bulb, *B*, and the pressure change noted. This expansion occurred when the mercury was

lowered from the porous disk, *C*, to the capillary at the bottom. Check determinations were possible by recompressing and re-expanding the helium.

The volume of the liquid to be adsorbed was measured in a dilatometer attached at *H*; the liquid was then introduced into the adsorption cell through a porous disk valve, *G*. The arm of this valve leading to the adsorption cell was capillary tubing, so no significant error was caused in the volume of the adsorption cell by slight variations in setting the mercury at a definite level above the porous disk.

Pressure measurements were made directly on a constant volume manometer at *I*. This manometer was constructed of 12 mm. tubing and was connected to the adsorption cell by a short length of capillary tubing. The total volume of the tubing above the zero level of the mercury that was external to the water bath was approximately 2 cc.. Since room temperature varied only 1° C. from the bath temperature, the error introduced here was probably less than that involved in the simultaneous setting of the two manometers in the previous apparatus.

The system was evacuated and helium was admitted through stopcock *J*.

The elimination of the cutoff between the expansion system and the adsorption cell, the use of capillary tubing, and the removal of the second manometer permitted a reduction in the ratio of the volume of the free space in the charcoal cell to the weight of charcoal to almost one-half of what it was in the previous apparatus. This factor alone decreased the absolute error in the measurement of the volumes to one-half.

An apparatus of this design is not suitable if sufficient adsorbate is present to exert a measurable vapor pressure.

## Results

### *Carbon Tetrachloride*

Over 50 determinations of the density of carbon tetrachloride adsorbed on charcoal were made. Typical results are presented in Table I. The variation of equilibrium pressure, the 'uncorrected' average layer density and the 'corrected' average layer density as functions of the weight adsorbed are shown in Figs. 2, 3, and 5, respectively. The uncorrected density is that computed from the expansion of helium neglecting the effect of vapor carry-over from the expansion system into the adsorption cell. This factor has been taken into consideration in computing the corrected density.

The results of Series 1 and 2 were obtained in the modified Morrison and McIntosh apparatus at a temperature of  $20.2 \pm 0.05^\circ \text{C}$ .; each point shown in Figs. 3 and 5 is the mean of from two to six determinations. The results of Series 3 were obtained in the second apparatus, which was described above, at a temperature of  $24.8 \pm 0.05^\circ \text{C}$ . Adsorption and desorption points are not shown separately, since in no instance was there any significant difference in either the equilibrium vapor pressure or the apparent density of the adsorbate.

TABLE I  
THE DENSITY OF ADSORBED CARBON TETRACHLORIDE

$x/m$ , gm./gm.	Series	Equilibrium pressure, cm.	Uncorrected density, gm./cc.	Corrected density, gm./cc.
0.0461	1		1.8	1.8
0.0468	2		1.8	1.8
0.0475	3		1.74	1.74
0.0925	3		1.35	1.35
0.234	3		1.39	1.39
0.234	2		1.41	1.41
0.235	1		1.42	1.42
0.467	1		1.40	1.40
0.469	2		1.42	1.42
0.478	2D		1.40	1.40
0.926	2D	0.31	1.53	1.46
0.929	1	0.37	1.48	1.43
0.940	2	0.45	1.52	1.47
1.29	1	1.23	1.60	1.51
1.32	2	1.35	1.59	1.52
1.45	2	3.02	1.70	1.51
1.50	2	5.24	1.77	1.53

D indicates desorption.

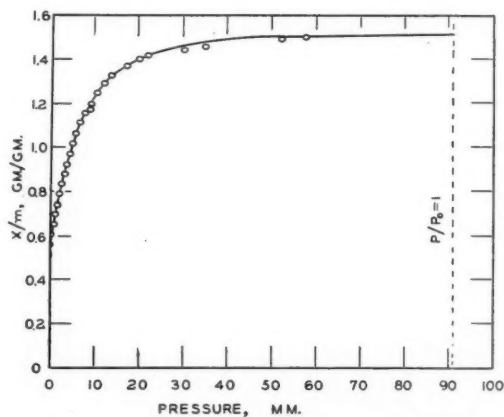


FIG. 2. The adsorption isotherm of carbon tetrachloride on charcoal at 20° C.

The curve of the uncorrected density versus weight adsorbed (Fig. 3) is of interest because of the striking similarity to the curve presented by Danforth and DeVries (3) for the carbon tetrachloride-charcoal system at 30° C. (Fig. 4). The density is high initially but drops abruptly to a minimum as  $x/m$  increases. On further increasing  $x/m$  the density increases, linearly at first, then more rapidly as  $x/m$  approaches the saturation value.

However, once the effect of vapor carry-over is taken into consideration (Fig. 5) the rapidly increasing portion of the curve disappears. The corrected apparent density of carbon tetrachloride does not exceed nor even approach the normal liquid density near saturation.

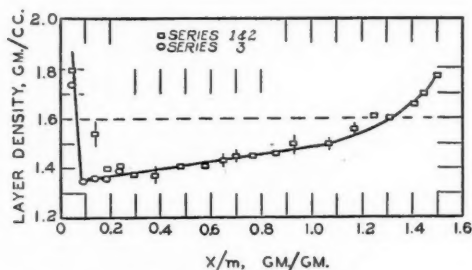


FIG. 3. Uncorrected apparent density of carbon tetrachloride adsorbed on charcoal at 20° C.

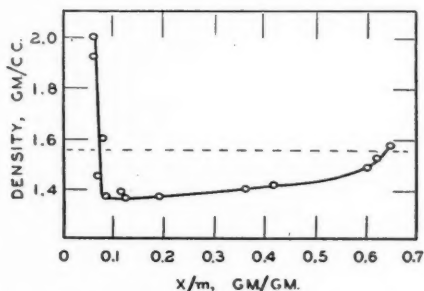


FIG. 4. Density of carbon tetrachloride adsorbed on charcoal at 30° C. according to Danforth and DeVries.

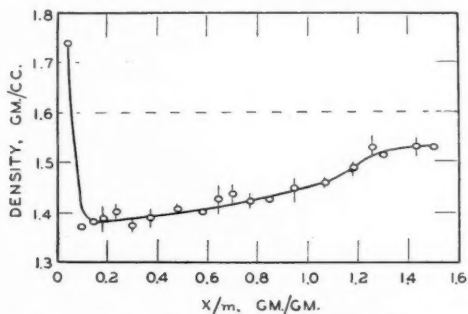


FIG. 5. Apparent density of carbon tetrachloride adsorbed on charcoal at 20° C.

The assumption that the final helium pressure is the final total pressure minus the initial vapor pressure is not valid. It is rather difficult to estimate the magnitude of the error introduced by this assumption. We would expect



that it would be related to the difficulty encountered by the vapor in diffusing back into the expansion system from the adsorption cell. Consequently, in the apparatus used in this investigation where diffusion had to take place through a length of capillary tubing and the porous disk of the cutoff, it is not surprising that the error reached serious proportions. In the apparatus used by Danforth and DeVries the error may have been much less; and error of 0.05 gm. per cc. does indicate some source of error.

Since the completion of this investigation on the carbon tetrachloride - charcoal system, Wiig (15) has suggested independently that vapor carry-over may have introduced a serious error in the measurements of Morrison and McIntosh on the water-charcoal system. In the latter system, hysteresis is an additional complication.

Danforth and DeVries (3) obtained a high density whenever the ratio of the quantity adsorbed to the quantity required for saturation was less than 0.12. The experimental results obtained here indicate that the density of the adsorbate is higher than the normal liquid density only when this ratio is less than 0.03—that is, when  $x/m$  is less than 0.05 gm. per gm.

An examination of the reproducibility of the results obtained in the first apparatus indicates that in any one determination the measured volume of the adsorbate may be in error by as much as 0.01 cc. per gm. of charcoal. Consequently at  $x/m = 0.15$  gm. per gm. the error may be as high as 10%; the actual numerical value obtained when small quantities of adsorbate are present have little significance. With the second apparatus the possible error appears to be 0.003 cc. per gm. of charcoal, indicating that the error could be 10% when  $x/m = 0.05$  gm. per gm. Consequently, even when  $x/m = 0.0475$  gm. per gm. the density of the adsorbate may not exceed the normal liquid density.

TABLE II  
THE DENSITY OF ADSORBED DIETHYL ETHER

$x/m$ , gm./gm.	Equilibrium pressure, cm.	Adsorbate density, gm./cc.
0.046	0.13	0.76
0.112	0.14	0.64
0.182	0.10	0.67 <sub>3</sub>
0.248	0.28	0.68 <sub>2</sub>
0.318	0.63	0.69 <sub>0</sub>
0.385	1.33	0.68 <sub>4</sub>
0.454	2.75	0.69 <sub>3</sub>
0.523	4.63	0.69 <sub>8</sub>
0.588	7.47	0.70 <sub>7</sub>
0.648	12.51	0.69 <sub>7</sub>
0.667	15.85	—
0.687	24.31	—
<i>Desorption</i>		
0.595	7.66	0.71 <sub>1</sub>
0.385	1.31	0.70 <sub>8</sub>
0.176	0.13	0.67 <sub>2</sub>

*Diethyl Ether*

The results obtained for the diethyl ether - charcoal system are tabulated in Table II. The adsorption isotherm is shown in Fig. 6; Fig. 7 is an enlarged section showing the discontinuity in the low pressure region. The variation of

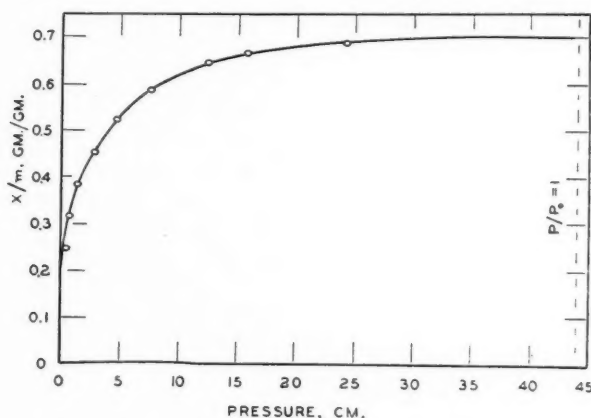


FIG. 6. Adsorption isotherm of diethyl ether on charcoal at 20° C.

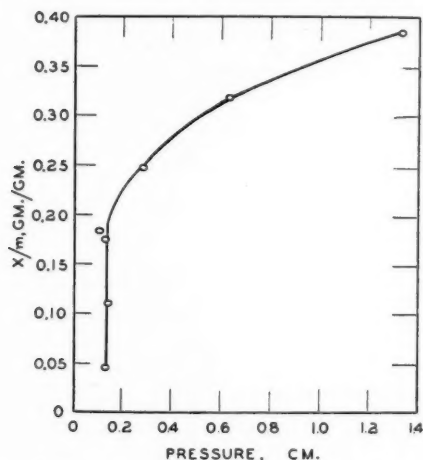


FIG. 7. Enlarged section of the low pressure region of Fig. 6.

the corrected apparent density of the adsorbed layer with  $x/m$  is shown in Fig. 8. Here again the density of the adsorbed layer is lower than the normal liquid density over the whole course of the isotherm, excepting possibly when only small quantities of adsorbate are present. In plotting these points it has been assumed that the possible error in determining the volume of the adsorbate

is 0.4 cc., i.e., 0.011 cc. per gm. of charcoal. Here again there is no evidence of hysteresis in either the equilibrium vapor pressure or the density.

The possible effect that the adsorption of helium would have on these measurements is dealt with below.

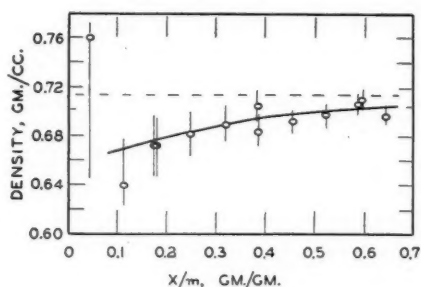


FIG. 8. Apparent density of diethyl ether adsorbed on charcoal at 20° C.

#### Neon

To a first approximation, in a liquid such as carbon tetrachloride, the molecules may be considered as rigid spheres arranged in close packing. The effective volume of each molecule is that of the molecule itself plus an appropriate proportion of the volume adjacent to it into which the neighboring molecules, because of steric factors, cannot penetrate. In the adsorbed state the molecules undoubtedly assume some type of arrangement on a surface which may or may not be continuous. We might expect the change in the volume of an adsorbent-adsorbate system when more adsorbate is added to depend to some extent on the gas used for measuring the change; even if other factors are absent the size of the gas molecules should have some effect since the smaller the molecule the more closely should it approach the adsorbed molecule. In an attempt to determine whether or not the apparent density of the adsorbate did depend on the measuring medium the volume of the free space in the

TABLE III

VOLUME OF ADSORPTION CELL AS MEASURED WITH NEON

Pressure on expansion-adsorption system, cm.	Pressure on adsorption cell, cm.	Volume of adsorption cell, cc.
24.28	52.92	119.14
21.30	46.48	118.88
15.50	33.80	119.03
11.86	25.88	118.9
8.57	18.78	118.0
5.69	12.45	118.3

adsorption cell of the second apparatus was measured using neon instead of helium. Typical results are shown in Table III.

The corresponding volume as determined using helium as the expanding medium was 110.21 cc., with an average deviation of 0.04 cc. This is the mean of 10 determinations, some of which were made immediately before and the remainder immediately after the measurements with neon.

On the assumption that helium is not adsorbed on charcoal it is possible to calculate the extent to which neon is adsorbed. These calculations indicate that

$$\frac{\Delta V}{\Delta P} = 0.00345 \text{ cc. per cm.,}$$

where

$\Delta V$  is the change in the volume of neon adsorbed in cubic centimeters at 76 cc. of mercury,

$\Delta P$  is the pressure change in centimeters of mercury.

If this relation extends to zero pressure, the volume of neon adsorbed on charcoal at 25° C. at any pressure is given by:

$$(\text{Pressure, in cm.}) \times (0.00345 \text{ cc. per cm.}).$$

This relation was used to compute the volume adsorbed at appropriate pressures between 15 and 26 cm., and the data obtained from the expansion of neon, some of which were given in Table III, were used to compute the volume adsorbed at higher and at lower pressures (Fig. 9).

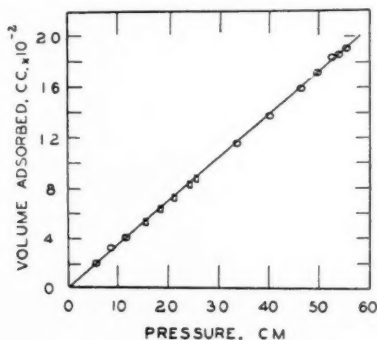


FIG. 9. Adsorption isotherm of neon on charcoal at 25° C.

It is interesting to note that according to data presented by Claude (2) very little error is introduced by assuming a linear relation between the volume of neon adsorbed on charcoal and the pressure up to 4 cm. at -195.5° C. Further, at this same temperature he has found that helium is adsorbed to one-thirtieth the extent of neon. If this is true, then at 25° C. and 50 cm. approximately  $5 \times 10^{-3}$  cc. of helium is adsorbed per gram of charcoal.

### Discussion

#### Carbon Tetrachloride - Charcoal System

In Figs. 10 and 11 the adsorption isotherm of carbon tetrachloride is plotted according to the Langmuir equation and the Harkins-Jura equation respectively.

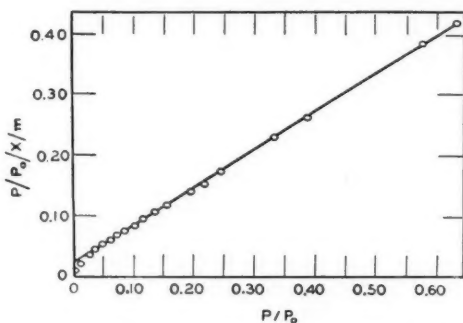


FIG. 10. Adsorption isotherm of carbon tetrachloride on charcoal plotted according to the Langmuir equation.

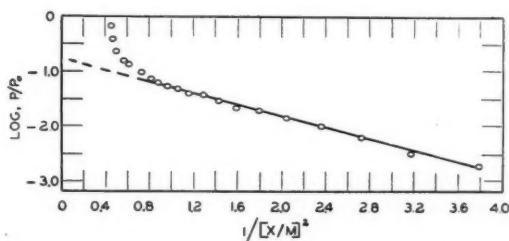


FIG. 11. Adsorption isotherm of carbon tetrachloride on charcoal plotted according to the Harkins-Jura equation.

The Langmuir plot is linear when  $P/P_0$  exceeds 0.04; this corresponds to  $x/m$  greater than 0.9 gm. per gm. When  $x/m$  is small the deviation is unmistakable. The Brunauer-Emmett-Teller multilayer equation is valid only from  $x/m = 0.9$  gm. per gm. to  $x/m = 1.4$  gm. per gm.

The Harkins-Jura plot is linear from the lowest vapor pressure measured ( $P/P_0 = 0.002$ ), where  $x/m = 0.5$  gm. per gm., to  $P/P_0 = 0.055$ , where  $x/m = 1.0$  gm. per gm. Jura and Harkins (9) suggest that with porous adsorbents the course of the isotherm at high relative pressures is governed, not by the equation of state of the adsorbate, but by the structure of the adsorbent. Fortunately, perhaps, when  $\log P/P_0$  is plotted as a function of  $1/(x/m)^2$  rather than  $1/(x/m)$  the linear portion of the curve is extended to  $P/P_0 = 0.118$  where  $x/m = 1.25$  gm. per gm.

If we accept the Harkins-Jura criterion for detecting gaseous and condensed films on solid subphases it is obvious that, at least when  $x/m$  exceeds 0.5

gm. per gm., we do not have the coexistence of vapor and condensed adsorbed phases in this system. This, then, cannot be the cause of the low apparent density of the adsorbate.

Indeed, from geometrical considerations we would expect a 'vapor' adsorbate to have a higher, rather than a lower, density than a 'liquid' adsorbate.

The density of carbon tetrachloride in the liquid state at 20° C. is 1.60 gm. per cc. If we consider that the molecules are rigid spheres and that they are closely packed in the liquid state, then the packing fraction is 0.74 and the density of carbon tetrachloride corrected for the void volume is 2.17 gm. per cc.

If we assume a highly idealized structure for the adsorbent we can compute what the density of a carbon tetrachloride molecule adsorbed on different types of sites would be. If a molecule were adsorbed on a pointed projection of the adsorbent, the change in the free space of the adsorption cell as measured by helium displacement would be the volume of an isolated molecule; the apparent density would approximate 2.17 gm. per cc. If adsorption occurred as a continuous monolayer on a plane surface, the effective volume of each molecule would be that of a hexagonal prism of height equal to the radius of the molecule plus that of a hemisphere; the apparent density on the basis of this volume would be 1.64 gm. per cc.

Consequently, if the molecules are closely packed as we would expect them to be in a 'liquid' phase, the density as measured by helium displacement would not differ greatly from that of the liquid state. However, if the molecules are widely separated as they would be in a 'vapor' phase, the density should more closely approach that calculated above for an isolated molecule. This is considerably higher than the normal liquid density.

It is well known that some of the internal voids of porous adsorbents are not accessible to large molecules. Guest, McIntosh, and Stuart (5), using a sample of this same charcoal, report that the density in helium is 1.96 gm. per cc. and in carbon tetrachloride is 1.85 gm. per cc. There is thus a total of 0.031 cc. per gm. of void volume inaccessible to carbon tetrachloride. This same factor may be important in the measurement of the density of an adsorbate since the adsorbed molecule may block off some of the voids and consequently lead to low density values. Until more is known concerning the structure of the charcoal it is difficult to correct for this factor. In Fig. 12 is shown the curve obtained when one of the many arbitrary choices is used. Here it has been assumed that when  $x/m$  exceeds 0.45 gm. per gm. the total void volume of 0.031 cc. has been blocked off so that the measured volume of the adsorbed layer is too high by this amount; when  $x/m$  is less than 0.45 gm. per gm. it has been assumed that the measured volume is too high by  $(0.031) \times \left(\frac{x/m}{0.45} \text{ cc.}\right)$ . There is discontinuity in this curve at approximately  $x/m = 1.0$  gm. per gm.; this, with the discontinuity which apparently exists at  $x/m = 0.45$  gm. per gm., divides the absolute density - weight adsorbed curve into three regions:



(a)  $x/m = 0$  to  $x/m = 0.45$  gm. per gm. where the blocked-off pore volume is proportional to the quantity of adsorbate present,

(b)  $x/m = 0.45$  to  $x/m = 1.0$  gm. per gm. where the blocked-off pore volume increases slightly or the absolute density of the adsorbate decreases slightly,

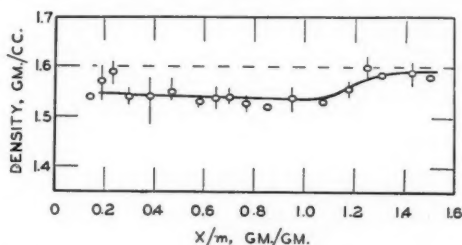


FIG. 12. Absolute density of carbon tetrachloride adsorbed on charcoal at 20° C.

(c)  $x/m = 1.0$  to  $x/m = 1.5$  gm. per gm. where either (1) the blocked-off pore volume decreases, or (2) some rearrangement occurs to a more dense packing of the adsorbate molecules, or (3) the density of the last 0.5 gm. per gm. of adsorbate is extremely high.

These regions correspond roughly to the three regions of the adsorption isotherm, for which

- (a) The equilibrium pressure is less than 0.02 cm., i.e., immeasurably low,
- (b) The Harkins-Jura equation is valid,
- (c) The Langmuir equation is valid.

Since the method used for computing the absolute density was chosen arbitrarily, it would appear preferable to examine the differential density values; the differential density is the derivative of the weight adsorbed-measured volume plot. When this is done the same three regions are apparent. (Table IV).

TABLE IV

DIFFERENTIAL DENSITY OF ADSORBED CARBON TETRACHLORIDE

—	$x/m$ , gm./gm.	Differential density, gm./cc.
(a)	0 - 0.5	1.40
(b)	0.5 - 1.0	1.50
(c)	1.0 - 1.4	1.77
(d)	1.4 - 1.5	1.53 Approximately

These changes in the differential density may be attributed either to rearrangements of the adsorbed molecules or to variations in the volume of the internal voids blocked off by the adsorbate.

One possible interpretation is as follows:

Region (a) indicates adsorption in pores where the adsorbed molecules block off an appreciable part of the pore;

Region (b) indicates that adsorption occurs next in larger pores where the fraction of pore volume blocked off is less important;

Region (c) indicates either (1) expansion of the charcoal, which permits penetration into hitherto inactive voids, or (2) the adsorption of the molecules on a plane surface.

When we consider the shape of the adsorption isotherm the second alternative appears unlikely. If adsorption were occurring on a plane surface, even if only a small fraction of the molecules were in the second and subsequent layers, the adsorption isotherm should obey the Brunauer-Emmett-Teller multilayer equation rather than the Langmuir equation. Since the Langmuir equation is valid in this high pressure region, adsorption probably occurs in restricted spaces.

#### *Diethyl Ether - Charcoal System*

The adsorption isotherm of diethyl ether on charcoal obeys the Langmuir equation when  $P/P_0$  exceeds 0.04 or  $x/m$  exceeds 0.40 gm. per gm. (Fig. 13). The Brunauer-Emmett-Teller multilayer equation is valid over a somewhat

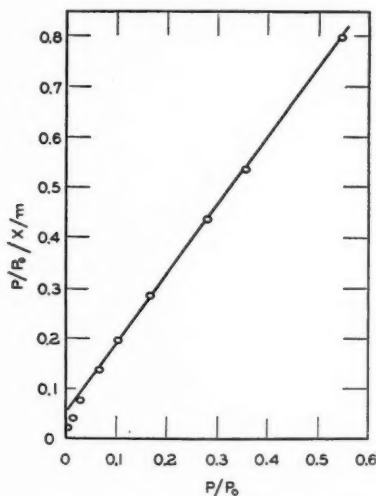


FIG. 13. Adsorption isotherm of diethyl ether on charcoal at 20° C. plotted according to the Langmuir equation.

narrower region. At  $x/m$  less than 0.4 gm. per gm. none of the common adsorption equations apply.

Even though there is no region of the isotherm where a linear relation exists between  $\log P/P_0$  and  $1/(x/m)^2$  the results are not necessarily inconsistent

with the Harkins-Jura theory. According to this theory the pressure is constant as the weight adsorbed increases whenever a first order phase change occurs. In the diethyl ether system the pressure remained constant at 0.13 cm. ( $P/P_0 = 3 \times 10^{-3}$ ) as  $x/m$  increased from 0.046 to 0.18 gm. per gm. A first order phase change does occur during the transition of a gaseous to a liquid film. If the liquid phase were a condensed liquid phase the Harkins-Jura equation would apply. However, a liquid expanded film may form first. In this event, as more adsorbate is added there should be a transition to a liquid intermediate and finally to a liquid condensed film. Evidence of the formation of a liquid condensed film was obtained in carbon tetrachloride-charcoal system but a deviation occurred from the Harkins-Jura equation at high relative pressures, presumably because of the porous nature of the adsorbent. With diethyl ether on charcoal, since over no region of the isotherm is the logarithm of the relative pressure a linear function of the reciprocal of the square of the quantity adsorbed, the influence of the adsorbent structure may have become dominant before the weight adsorbed was sufficiently great to cause the formation of a liquid condensed film.

The preliminary results obtained for the density of diethyl ether on charcoal indicate that the relation between the density and the weight adsorbed possesses the same general characteristics as the corresponding relation for the carbon tetrachloride-charcoal system. According to Guest, McIntosh, and Stuart (5) this charcoal has a density in helium of 1.96 gm. per cc. and in diethyl ether 1.94 gm. per cc.; the void volume inaccessible to diethyl ether is thus 0.006 cc. per gm. of charcoal. If we assume that the apparent volume of the adsorbate, as computed from the smoothed curve in Fig. 8, is too high by 0.006 cc., the absolute density-weight adsorbed curve so obtained is divided into three regions:

- (a) When  $x/m$  is less than 0.2 gm. per gm. the density is constant at approximately 0.694 gm. per cc.,
- (b) As  $x/m$  increases from 0.2 to 0.4 gm. per gm. the density increases to approximately 0.707 gm. per cc.,
- (c) As  $x/m$  increases above 0.4 gm. per gm. the density remains constant at 0.707 gm. per cc. This is the region over which the Langmuir equation applies.

It was postulated above that the increase in the absolute density of adsorbed carbon tetrachloride is due to the expansion of the charcoal and the penetration of the adsorbate into hitherto unavailable voids. If this is true for the diethyl ether-charcoal system we would expect the charcoal to expand when  $x/m = 0.20$  gm. per gm. or when the ratio of the weight adsorbed to the weight required for saturation was 0.3. Haines and McIntosh (6) have measured the length change of a rod of zinc chloride activated charcoal during the adsorption of dimethyl ether at 6.5° C. The rod underwent an initial contraction and then expanded as the quantity adsorbed was increased. The maximum contraction occurred when 150 cc. had been adsorbed and the

volume required for saturation was somewhat greater than 550 cc. The ratio here is about 0.3. Although the two systems are not identical we might expect some degree of similarity between the adsorption of dimethyl ether and diethyl ether on two samples of zinc chloride activated charcoal from the same company.

#### *Possible Effect of Helium Adsorption on the Measurements*

It is generally assumed that helium is not adsorbed on charcoal at room temperature. This assumption is based mainly on the work of Homfray (8) who reports that at 48.4 cm. of mercury and 290° A. the volume of helium adsorbed on 3 gm. of charcoal is 0.00 cc. Others, who have measured the volume of a cell of activated charcoal by the method of helium expansion, have assumed that since the apparent volume is independent of the helium pressure, this is a positive indication that helium is not adsorbed. However, so long as the volume adsorbed is a linear function of the pressure, this method yields absolutely no information as to the extent to which adsorption occurs.

It was shown above that at 50 cm. pressure and 25° C. it is possible that  $5 \times 10^{-3}$  cc. (computed at one atmosphere pressure and 25° C.) of helium was adsorbed on a gram of this charcoal. Small though this may be, it is sufficient to cause an error of 0.01 cc. per gram of charcoal present when the volume of the free space in the adsorption cell is determined. What effect vapors have on the adsorption of helium is unknown. Until more accurate data are available on the adsorption of helium, the values obtained for the density of charcoal or the density of an adsorbate, using the technique of helium displacement, are subject to some degree of doubt.

#### **Acknowledgments**

One of the authors (M. T.) would like to acknowledge the valuable assistance given during the preliminary stages of this investigation by Dr. J. A. Morrison of the National Research Council, Ottawa. The apparatus used for the greater portion of the experimental work was designed by Dr. Morrison, and was built, in part, from that employed by him for the study of the charcoal-water system. Lastly, thanks are due to Dr. Morrison for his advice on technique and his directions for the construction and use of the apparatus.

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## THE FLOW OF GASES AND VAPORS THROUGH ADSORBING POROUS MEDIA<sup>1</sup>

BY R. H. TOMLINSON AND E. A. FLOOD

### Abstract

The flow rates of gases and vapors through highly activated charcoal rods have been measured. The results obtained indicate that a new phenomenon has been discovered. While the flow rates of gases that are not highly adsorbed can be satisfactorily correlated by the Adzumi equation and other equations of similar mathematical form, it has been found that the strongly adsorbed vapors of diethyl ether and ethyl chloride pass through the charcoal rods at rates considerably in excess of those required by known equations. To explain the results it appears necessary to resort to mechanisms quite outside of those usually considered in the application of kinetic theory to problems associated with passage of gas through porous diaphragms. The simplest and most direct of such mechanisms involves mobility of the adsorbed material. It is particularly striking that the flow rate of diethyl ether through activated charcoal rods has been found to be greater than that of helium in pressure regions where relative rates of flow of gases through non-adsorbing porous diaphragms are dominated by inverse square root molecular weight ratios. The measurement of gaseous flow rates through porous media are rendered the more difficult where appreciable adsorption occurs. The experimental methods are described in detail, sources of error are discussed, and results presented for the gases helium, hydrogen, nitrogen, carbon dioxide, diethyl ether, and ethyl chloride.

### Introduction

#### (a) Historical

Fluid flow through various porous media has been the subject of extensive investigations which have included studies of the permeabilities of a wide variety of materials. To fit experimental results many empirical and semi-empirical equations have been developed. None of these equations provide a factor that is a function of the quantity of gas adsorbed. One might expect that, in the case of a porous material having micropores most of which were capable of being filled by sorption, the permeability of the material to sorbable gas would be much less than its permeability to non-sorbable gas.

The flow of gases through a bed of charcoal grains has received considerable attention from various researchers, but the gaseous flow through an activated carbon rod has not been thoroughly investigated. Hatfield (7) has measured the flow of gases through porous carbon rods, but these rods were not activated. Hodgins, Flood, and Dacey have made a few preliminary measurements of gas flow through a carbon rod of a type similar to that used in the researches reported here, but their findings have not been published.

If the flow rate is to be in any sense characteristic of the fine grained structure of a porous material, it is, of course, essential that the porous material be free from adventitious cracks, holes, and other mechanical faults not characteristic of the porous medium. It will be immediately obvious that any

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relatively large hole or crack would make such a large contribution to the total flow rate that it would completely mask the flow phenomena associated with the inherent structure. It is very difficult to obtain charcoal free from such adventitious cracks. Many types of charcoal activation yield activated carbon granules with relatively large visible fissures. However, such processes as the zinc chloride extrusion type activations yield activated carbon rods of remarkably uniform structure. The experiments reported in this paper were conducted with this type of charcoal.

The experimental difficulties in measuring flow rates through the charcoal rods used are complicated by three main factors:

- (1) The flow rates are very low.
- (2) The attainment of a steady state of flow is considerably complicated by adsorption. It is necessary that in the final steady flow the quantity of material flowing in and out of every element of length in the path of the flow be identical. From this it is apparent that no decay rate apparatus can be used to measure the flow rate, since it involves continuously changing input and output pressures, and therefore a complex set of changing adsorption-desorption conditions within the charcoal.
- (3) The small changes in volume of the charcoal rod accompanying adsorption and desorption make it necessary to provide a flexible type of gas tight seal not easily obtained with charcoal rods.

(b) *Theoretical*

The theory of flow through a porous diaphragm is very complicated. This is accentuated by our inexact knowledge of the shape, size, and structure of the pores. The equations relating to the flow through such materials must of necessity be empirical and involve many assumptions. It is interesting to note that most of these equations are equivalent and that simple substitutions will transform one type to another. For example the Kozeny equation (10) may be regarded as the Poiseuille equation applied to granular beds, while the Poiseuille equation may be regarded as a special case of an equation put forward by Maxwell (11) based on the kinetic theory of slip, and of the somewhat similar equation of Knudsen (9). The general equation of Knudsen reduces to the equation describing what is generally known as Knudsen flow.

One of the most satisfactory equations expressing the relative rates of flow of various gases through porous media is that proposed by H. Adzumi (1, 2, 3, 4). Adzumi considers the flow through porous media to be the summation of the flows in a large number of capillaries in series and in parallel with each other. Although Adzumi starts to develop the theory leading to his equation in a rigorous mathematical manner, he introduces a succession of approximations that result in a final equation that is largely empirical.

$$K = \frac{\pi n \bar{r}^4 \bar{P}}{8 \eta l} + \gamma \frac{4}{3} \sqrt{2\pi} \sqrt{\frac{R_0 T}{M}} \frac{n \bar{r}^3}{l}, \quad (1)$$

where  $K = \frac{VP}{\Delta P}$ ,

- $V$  = Volume flow per unit time,  
 $P$  = Pressure at which  $V$  is measured,  
 $\Delta P$  = Pressure gradient across the porous system,  
 $\bar{P}$  = Mean pressure defined by  $\frac{P_1 + P_2}{2}$ , where  $P_1$  and  $P_2$  are the pressures at the high and low pressure ends of the sample respectively,  
 $n$  = Number of capillaries in parallel,  
 $\bar{r}$  = Mean radius of the pores,  
 $l$  = Mean length of the capillaries,  
 $R_0$  = The gas constant,  
 $T$  = The absolute temperature,  
 $M$  = Molecular weight,  
 $\eta$  = Viscosity of the gas,  
 $\gamma$  is a term due to the coefficient of slip, which numerically should not vary significantly from 0.9 (1).

The various numerical constants in Equation (1) cannot, of course, be taken literally since most porous material is made up of channels that are not of constant radius, and in fact the capillaries are not circular in cross section. Equation (1) may be written in the form:

$$K = \frac{A}{\eta} \bar{P} + B \sqrt{\frac{T}{M}}, \quad (2)$$

where  $A$  and  $B$  are constants that are characteristic of the porous material and  $\eta$  and  $M$  are characteristic of the fluid.  $\bar{P}$  and  $T$  are variables representing experimental conditions. While it is known from the work of Knudsen, Gaede, and others that this form of equation does not describe the rate of flow accurately at low pressure, the equation fits the facts quite closely over a very considerable range of higher pressures. Consequently at higher pressures the flow through a collection of capillaries should also have this form. However, if an appreciable fraction of the total flow is through spaces of cross-sectional dimensions comparable to the mean free path of the gas molecules, we might expect the departure from the straight line plot to extend to higher pressures. (It may be seen from Equation (2) that for a given gas at constant temperature a plot of  $K$  against  $\bar{P}$  should give a straight line.)

From Equation (2) it may be concluded that if both the porous system and the temperature are kept constant, the variation in flow from one gas to another should be such that the slope of the flow vs. mean pressure plot should vary inversely as the viscosity of the gas, and the intercept on the flow axis should vary inversely as the square root of the molecular weight of the gas. From this it follows that if the flow of any gas at a given temperature is known as a function of the mean pressure, the flow of any other gas may be calculated.

Referring to Equation (1), the apparent mean radius,  $\bar{r}$ , and the effective number of pores,  $n$ , may be calculated (2, 3, 4). The mean radius calculated in this way is largely fictitious, but has been shown by Arnell (5) to be

theoretically almost equivalent to the hydraulic radius. In spite of the theoretical shortcomings of the Adzumi equation, it has been used with very considerable success to predict the relative flow rates of various gases through porous material.

### Experimental

#### (a) Materials

The activated carbon rods used in the work reported here were prepared by the National Carbon Company, and supplied through the courtesy of the Chemical Warfare Laboratories, Ottawa. The charcoal has the following general characteristics:

Helium density,  $2.22 \pm 0.05$  gm. per cc.

Mercury density,  $0.707 \pm 0.001$  gm. per cc.

Void fraction, 0.68 (calculated from mercury and helium densities).

Void fraction at saturation with diethyl ether, 0.24 (assuming the density of the adsorbed ether is equal to the density of liquid ether at the same temperature).

Adsorption surface areas by Brunauer, Emmett, and Teller method.

(a) Nitrogen, 1100 sq. m. per gm.

(b) Diethyl ether, 1200 sq. m. per gm.

(c) Ethyl chloride, 900 sq. m. per gm.

Permeability surface area, 64 sq. m. per gm. (Arnell method, assuming  $\alpha = \epsilon(5)$ ).

Pore radius,  $8.55 \times 10^{-5}$  cm. (method of Adzumi (2, 3, 4)).

Number of pores per unit volume,  $1.16 \times 10^6$  (method of Adzumi (2, 3, 4)).

All permeability data reported here are based on charcoal rods of length  $1.00 \pm 0.02$  cm. and diameter 0.38 cm.

#### (b) The Apparatus

Fig. 1 illustrates the apparatus that was used for measuring the flow rates of gases through a charcoal plug. In principle it is similar to that described by Hodgins *et al.* (8). It has, however, several variations. Manometer *J* reads directly the difference in pressure between the two ends of the charcoal plug and therefore ensures a constant pressure gradient across the sample. The pressure gradient may be varied by changing the amount of mercury in manometer *J* by addition or removal of mercury from the reservoir, *S*. This scheme requires only a ground terminal, *T*, and a single contact, *I*, in order to allow of a complete range of working pressure gradients. The contact, *I*, was made of tungsten filament wire, which was found to be less easily wetted by mercury than platinum. The tungsten contact therefore ensures of more sensitive make and break between it and the mercury.

To increase the sensitivity of the flow measurement from the rise of mercury in the burette, *K*, the volume of the manifold between the burette and the inlet side of the charcoal plug was kept to a minimum. The pressure of the

bulb, *C*, was maintained constant during any run by small manual adjustments of the mercury in burette *B*. This pressure was measured absolutely on manometer *A*, which was observed by means of a cathetometer. The

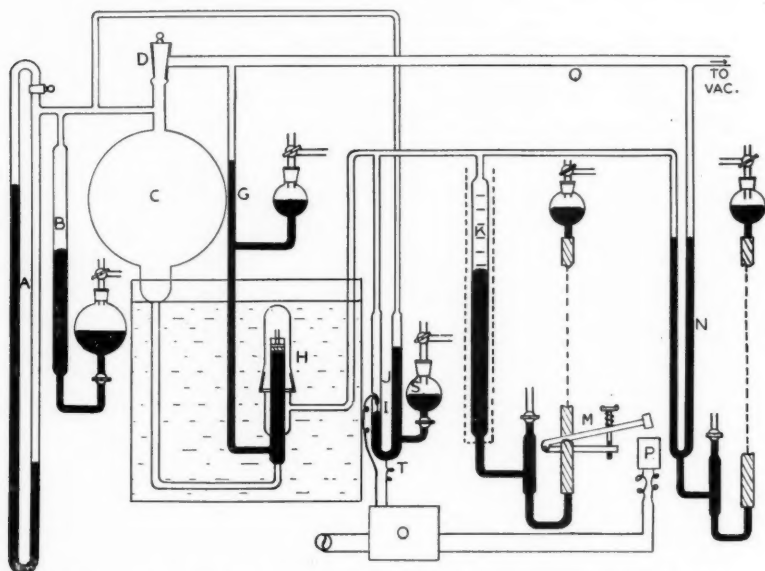


FIG. 1. Apparatus for measuring the flow rate of gases through a charcoal rod.

pressure of the gas in burette *K* is obtained by the addition of the pressure of the gas in manometer *A* and the pressure read from differential manometer *J*. By the use of a mercury cut-off, *N*, all stopcocks have been eliminated from the section of the apparatus where the flow measurements are read. This ensures that any flow measured from burette *K* represents flow into the charcoal.

To measure the flow rate of a gas through a sample mounted in the cell, *H*, the pure gas is allowed to enter the whole system through the manifold, *Q*, until the desired pressure for the low pressure end of the sample is gauged on manometer *A*. Stopcock *D* is then closed and further gas is admitted to the apparatus connected to burette *K* until manometer *J* shows the desired pressure gradient,  $\Delta P$ . The amount of mercury in manometer *J* is then adjusted from reservoir *S* until the contact, *I*, just touches the meniscus of the mercury. The mercury cut-off, *N*, is then closed and the rate of mercury rise in burette *K* that is required to maintain constant pressure on manometer *J* is observed. This pressure is maintained automatically by means of a pinch cock, *M*, solenoid, *P*, and electronic relay, *O*, as described by Hodgins *et al.* (8). The rate of rise of mercury in burette *K* is then a measure of the flow of gas into the charcoal under the conditions of temperature and pressure

observed. All recorded data have been observed for a measured volume change of at least 50 ml. or for a two hour period. For the adsorbable vapors as much as six or eight hours is required to establish a constant rate of flow into the charcoal. It is only after the rate has become constant that data have been recorded here. The non-stationary state of flow will be considered in another paper.

(c) *The Plug Holder*

Detail of the cell, *H*, Fig. 1, is shown in Fig. 2. This represents the method by which the charcoal rod is held in order that the gas flow through it may be measured. The charcoal rod, *A*, is held between the two gas leads, *B*

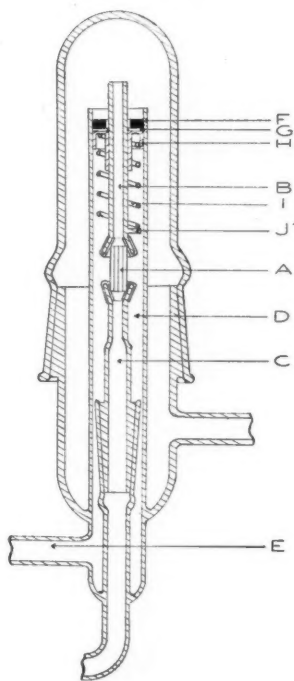


FIG. 2. Apparatus for holding a charcoal plug.

and *C*, which have funnel-shaped ends lined with a thin coat of rubber (about 3/1000 in. thick) to ensure both a minimum contact and tight seal between them and the charcoal rod. Compartment *D* is filled with mercury. This mercury is under pressure, which is applied through the pressure arm (Fig. 2, *E*; Fig. 1, *G*) so that there is always a minimum of 40 cm. of mercury pressure surrounding the wall of the charcoal rod. Since the pressure arm is connected to the system, Fig. 1, *G*, the 40 cm. mercury pressure on the charcoal wall is always in excess of the pressure of the gas in the system. The mercury

in compartment *D* is confined by Wood's metal, *F*, metal washer, *G*, and hollow-stemmed mushroom-shaped rubber washer, *H*. This allows of a short gas lead, *B*, for otherwise the mercury would seek the level of the mercury in the pressure arm. The Wood's metal is sealed to the wall of compartment *D*, but not the gas lead, *B*. In this way the gas lead, *B*, is free to move up and down through the metal washer, *G*. The rubber washer, *H*, forms a tighter seal with both the compartment, *D*, wall and the gas lead, *B*, as the mercury pressure is increased. It therefore allows the gas lead, *B*, freedom of motion, and at the same time prevents the mercury from attacking the Wood's metal. A steel spring, *I*, thrusts down on lug *J* attached to the gas lead, *B*, ensuring a tight fit between the gas lead, *B*, and the end of the charcoal.

This system was devised as the result of considerable research that showed that it was necessary to allow for the small volume changes that accompany adsorption and desorption on the charcoal rod. The necessity of surrounding the charcoal with mercury under a head of 40 cm. is shown by the following experiment.

TABLE I

· VARIATION IN APPARENT FLOW RATE OF NITROGEN THROUGH CHARCOAL RODS WITH CHANGE IN MERCURY PRESSURE ON THE WALL OF THE PLUG

$\bar{P}$  = 700 mm. mercury,  $\Delta P$  = 50 mm. mercury, and  $T = 308^\circ \text{K}$  for all runs. Flow measured in  $K'$  units =  $\frac{VP}{\Delta P}$ ,  $V$  = cc. per min.

Plug number	Flow in $K$ units	Mercury pressure, cm.
9	1.37	55
	1.37	12
10	4.54	2
	3.32	7
	2.24	12
	1.73	17
	1.62	22
	1.42	32
11	2.67	2.5
	2.27	7.5
	1.67	12.5
	1.42	17.5
	1.48	22.5
	1.34	32.5
	1.35	42.5
	1.36	11.0

The data in Table I, which are shown graphically in Fig. 3, represent the flow of nitrogen through plugs 9, 10, and 11 with variation of mercury pressure on the walls of the charcoal rod. Above 35 cm. mercury pressure the flow becomes independent of the pressure. It is concluded from these data that for pressures up to 35 cm. there is a component of flow between the mercury and the charcoal rod, and this flow is eliminated at higher pressures. Plug 9 (Curve 3) was subjected to high mercury pressure first, and there was no



increase in flow as the pressure was reduced. With plug 11 (Curve 1) the flow decreased as the pressure was increased up to 35 cm., but there was no increase in flow as the pressure was reduced. Since the flow does not increase

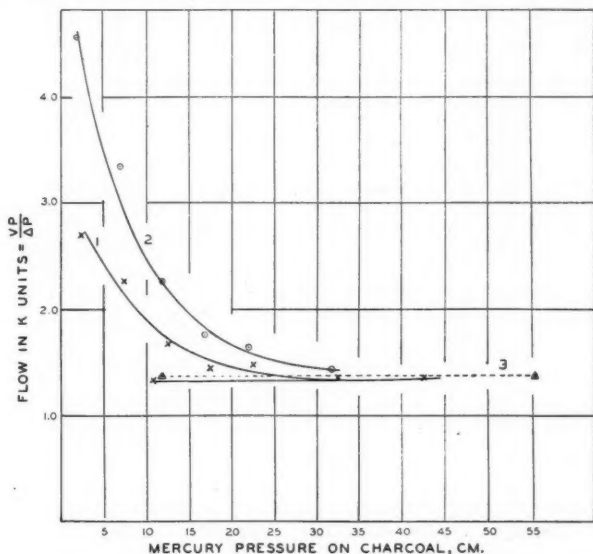


FIG. 3. Variation in apparent flow rate of nitrogen through charcoal rods with change in mercury pressure on the wall of the plug.

as the pressure is reduced, it is concluded that the mercury does not pull away from the irregularities of the surface once it has penetrated them. Examination of a charcoal rod subjected to mercury pressure shows traces of mercury held on the surface; this tends to uphold this theory. No sign, however, of mercury was found within such a sample. Curve 2 shows the flow through plug 10 as a function of the surrounding mercury pressure. All subsequent flow measurements were obtained with a minimum mercury pressure around the charcoal of 40 cm.

Table II gives the equations of the flow of nitrogen through six different samples of charcoal at 35° C. as a function of the mean pressure. The flow of nitrogen through plugs 12 and 14 are plotted fully in Figs. 4 and 5, respectively, thus showing the variation of individual measurements from the statistical lines of best fit. Plug 13 is considered to have had a real fissure or hole in it, but no such defect was visible to the eye or low power lens. Some of the variation of the flow from sample to sample would certainly be due to an end effect governed by the contact between the charcoal and the rubber gaskets, which seal the charcoal to the glass flanges. These data give satisfactory evidence that the charcoal is quite uniform, and therefore the flow data obtained is a characteristic of the charcoal structure.

### Experimental Results

Using the apparatus and technique described above, the rate of flow of the gases nitrogen, helium, hydrogen, and carbon dioxide were measured through

TABLE II

FLOW OF NITROGEN THROUGH SIX SAMPLES OF CHARCOAL ROD AS A FUNCTION OF THE MEAN PRESSURE IN MILLIMETERS OF MERCURY

Flow rates measured at 35° C. in  $K'$  units =  $\frac{V'P}{\Delta P}$ , where  $V'$  = cc. per min. per cm. length of charcoal

Plug number	Flow in $K$ units
9	$0.00118\bar{P} + 0.455$
10	$0.00125\bar{P} + 0.465$
11	$0.00123\bar{P} + 0.460$
12	$0.00120\bar{P} + 0.445$
13	$0.00200\bar{P} + 0.55$
14	$0.00119\bar{P} + 0.450$

TABLE III

FLOW RATES OF VARIOUS GASES THROUGH PLUG 12 AT 35° C.

$\Delta P = 50$  mm. mercury except where indicated. Flow measured in  $K$  units =  $\frac{VP}{\Delta P}$ , where  $V$  = cc. per min.

Flow rate	Mean pressure, mm. Hg	Flow rate	Mean pressure, mm. Hg
<i>Nitrogen</i>		<i>Carbon dioxide</i>	
1.29	685.2	1.30	679.0
1.23	632.4	1.08	515.6
1.03	466.9	0.93	412.0
0.905	360.4	0.79	306.5
0.733	226.9	0.65	202.0
0.642	153.3	0.58	154.7
0.613	117.3	0.53	114.0
0.504	63.7	0.44	66.4
0.476	43.2	—	—
0.440	24.0	—	—
0.420	11.9 <sup>a</sup>	—	—
<i>Helium</i>		<i>Hydrogen</i>	
1.94	706.0	3.30	686.0
1.81	588.4	3.02	580.2
1.72	487.8	2.76	476.5
1.58	372.5	2.54	376.8
1.47	279.8	2.26	268.7
1.33	182.0	2.00	160.0
1.22	109.6	1.82	103.0
1.10	25.0	1.57	25.0

<sup>a</sup>23.8 mm. gradient.

plug 12. The results are given in Table III and shown graphically in Fig. 4. The broken lines in Fig. 4 are drawn to give the best fit to experimental data, and the unbroken lines are calculated from the Adzumi equation using the

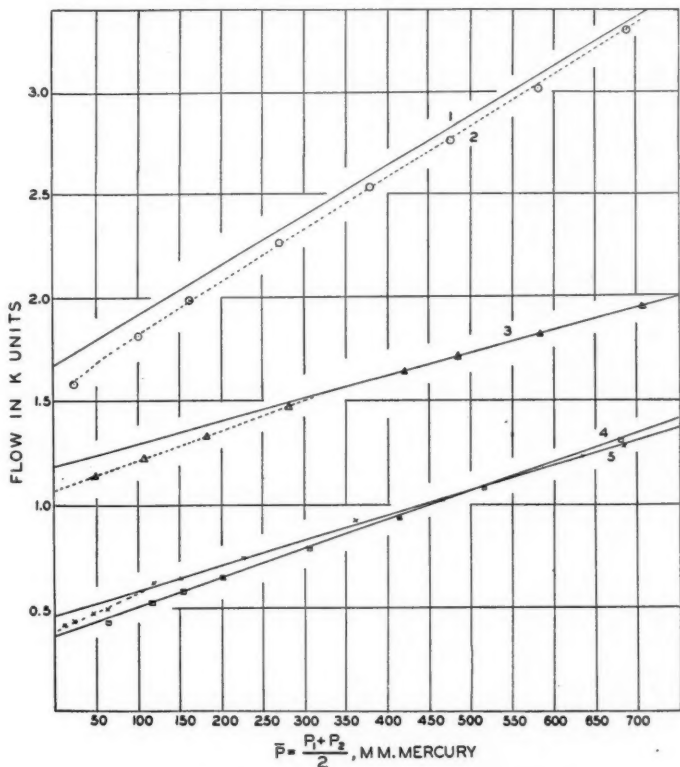


FIG. 4. Flow rates of various gases through plug 12 at 35° C.

Curve 1: Calculated hydrogen flow rate.

Curve 2: measured hydrogen flow rate.

Curve 3: helium flow rate.

Curve 4: carbon dioxide flow rate.

Curve 5: nitrogen flow rate.

best available viscosity and molecular weight data (Table IV). The nitrogen flow is taken as the basis for these calculations. It is apparent that the straight line plot expected from the Adzumi equation when  $K$  is plotted against  $\bar{P}$  does not hold exactly throughout the whole pressure range observed. In the cases of nitrogen and helium, the flow at low mean pressures is less than would be expected if we consider the flow at higher pressures to be on the straight line plot.

In the case of hydrogen the flow was less than that predicted throughout the whole pressure range where flow measurements were observed, but at higher pressures the deviation is not great. It would seem safe to assume

TABLE IV  
PHYSICAL PROPERTIES OF THE GASES USED

Gas	Molecular weight	Viscosity at 35° C., micropoises
Carbon dioxide	44.0	156.0
Diethyl ether	74.1	77.4
Ethyl chloride	64.5	105
Helium	4.0	202.5
Hydrogen	2.02	90.3
Nitrogen	28.0	181.5

that at even higher mean pressures the flow of hydrogen would have been the same as the predicted flow, and that the observed points recorded here would have been equivalent to the low pressure deviations shown by helium and nitrogen. This, however, should be checked experimentally. Carbon dioxide, although it is adsorbed to a moderate extent, did not show any deviation from the flow expected on the basis of the nitrogen flow through the charcoal.

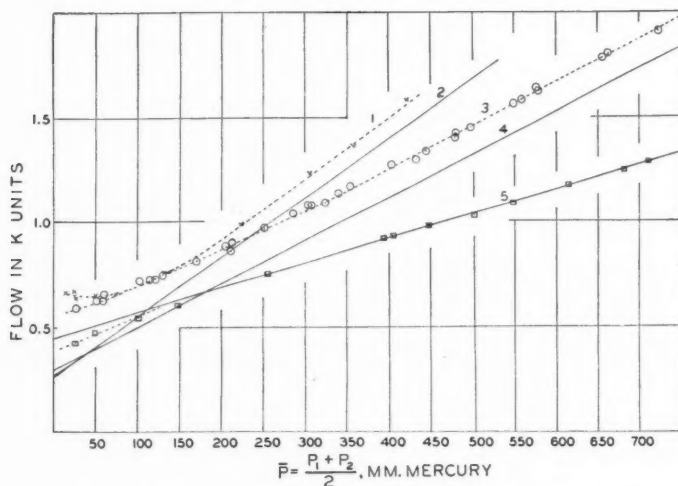


FIG. 5. Flow rates of various gases and vapors through plug 14 at 35° C.

- Curve 1: measured diethyl ether flow rate.
- Curve 2: calculated diethyl ether flow rate.
- Curve 3: measured ethyl chloride flow rate.
- Curve 4: calculated ethyl chloride flow rate.
- Curve 5: nitrogen flow rate.

TABLE V

FLOW RATES OF VARIOUS GASES AND VAPORS THROUGH PLUG 14 AT 35°C.

$\Delta P = 100$  mm. mercury except observations marked with a superscript *a* where  $\Delta P = 50$  mm. mercury. Flow rates measured in *K* units =  $\frac{VP}{\Delta P}$ , where *V* = cc. per min.

Flow rate	Mean pressure, mm. Hg	Flow rate	Mean pressure, mm. Hg
<i>Nitrogen</i>		<i>Ethyl chloride</i>	
1.29	711.1	1.91	724.0
1.25	689.0	1.80	665.0
1.18	615.0	1.78	656.1
1.09	549.2	1.62	680.5
1.03	502.9	1.63	578.4 <sup>a</sup>
0.980	448.7	1.58	559.5
0.930	405.4	1.56	554.8
0.915	394.4	1.45	449.0
0.750	255.4	1.42	480.6
0.607	147.5 <sup>a</sup>	1.40	480.4 <sup>a</sup>
0.543	103.0	1.33	446.7
0.475	49.9	1.30	432.7
0.427	25.0 <sup>a</sup>	1.27	405.3
<i>Diethyl ether</i>		1.17	355.0
		1.14	340.0
		1.09	325.3
		1.08	308.4
		1.07	305.7 <sup>a</sup>
		1.04	285.6
		0.970	251.0
		0.899	214.2 <sup>a</sup>
		0.866	213.0 <sup>a</sup>
		0.889	204.0
		0.815	171.0
		0.747	125.6
		0.724	117.2 <sup>a</sup>
		0.723	114.8 <sup>a</sup>
		0.720	101.5
1.57	421.2	0.633	58.0
1.35	359.7 <sup>a</sup>	0.651	58.2 <sup>a</sup>
1.23	306.6 <sup>a</sup>	0.625	51.0
0.995	225.4 <sup>a</sup>	0.591	25.0 <sup>a</sup>
0.755	134.6 <sup>a</sup>		
0.658	71.5 <sup>a</sup>		
0.645	50.0		
0.630	25.0 <sup>a</sup>		
0.673	25.0 <sup>a</sup>		
0.665	12.5 <sup>b</sup>		

<sup>b</sup> 25 mm. gradient.

The flow of nitrogen, diethyl ether, and ethyl chloride through plug 14 were measured at various mean pressures. The results are tabulated in Table V and shown graphically in Fig. 5. The unbroken lines (Curves 2 and 4) show the predicted flow for diethyl ether and ethyl chloride, respectively, based on the Adzumi equation using nitrogen data to determine the constants *A* and *B* (Equation 2). The broken lines (Curves 1 and 3) show the observed equilibrium flow rates. At low mean pressures the flow of the vapors of diethyl ether and ethyl chloride are twice as great as the predicted flow, and in the case of the diethyl ether, the flow appears to be increasing as the mean pressure is reduced. At higher mean pressures the flow of ethyl chloride and diethyl ether are greater than that predicted by an almost constant small amount.

Since it is necessary to know the adsorption characteristics of the activated carbon rods used for the flow experiments, adsorption isotherms were determined at 35° C. for the gases ethyl chloride and diethyl ether. The experimental results are presented in Table VI and represented graphically in Fig. 6. The nitrogen adsorption isotherm at 90° K was determined in order

TABLE VI  
ADSORPTION ISOTHERMS OF ETHYL CHLORIDE AND DIETHYL ETHER ON CHARCOAL AT 35° C.

Ethyl chloride, $x/m$ , gm./gm.	Pressure, mm. Hg	Diethyl ether, $x/m$ , gm./gm.	Pressure, mm. Hg
0.0316	0.45	0.2398	10.1
0.0864	2.85	0.3107	48.8
0.1507	10.55	0.348	102.8
0.234	36.15	0.378	166.6
0.290	75.35	0.395	280.3
0.332	129.9	0.405	352.4
0.375	214.1	0.410	376.0
0.414	313.9	—	—
0.447	417.4	—	—
0.478	558.3	—	—
0.490	715.5	—	—

to calculate the surface area of the charcoal by the method of Brunauer, Emmett, and Teller. The apparent densities of the charcoal rods in mercury and in helium were measured in order to obtain the void fraction of the charcoal.

### Discussion

The deviation of the flow of the permanent gases from the flow calculated on the basis of the Adzumi equation is not surprising when the numerous approximations in its derivation are considered. It is, however, notable that in the flow through a single uniform capillary Knudsen (9), Gaede (6), and others have observed that the flow, when plotted in the same manner as that used for the results presented here, did not give a straight line. It was observed that at pressures where the mean free path of the molecule was approximately equal to the capillary radius, the flow deviated from the straight line plot in much the same fashion as was observed with the charcoal. At still lower pressures, however, they found other changes occurring for which there are no comparable data obtained with charcoal. Although these phenomena have been studied exhaustively for many years, only semiempirical theories have been proposed to account for them.

Of greater interest is the deviation of the flow of the adsorbable vapors from the calculated values. The increased flow rate is even more surprising when one considers that, in the process of adsorption, sufficient vapor is held within the charcoal, so that if we consider it to be in the liquid phase, most of the void space would be filled. The charcoal is 68% voids as calculated from the

helium and mercury densities. If we consider that the diethyl ether is in the liquid state when it is adsorbed, only 24% voids remain at saturation. We can therefore see that at saturation a large portion of the void space in the charcoal is occupied, although at pressures below saturation we should expect greater fractions of the void space to be available.

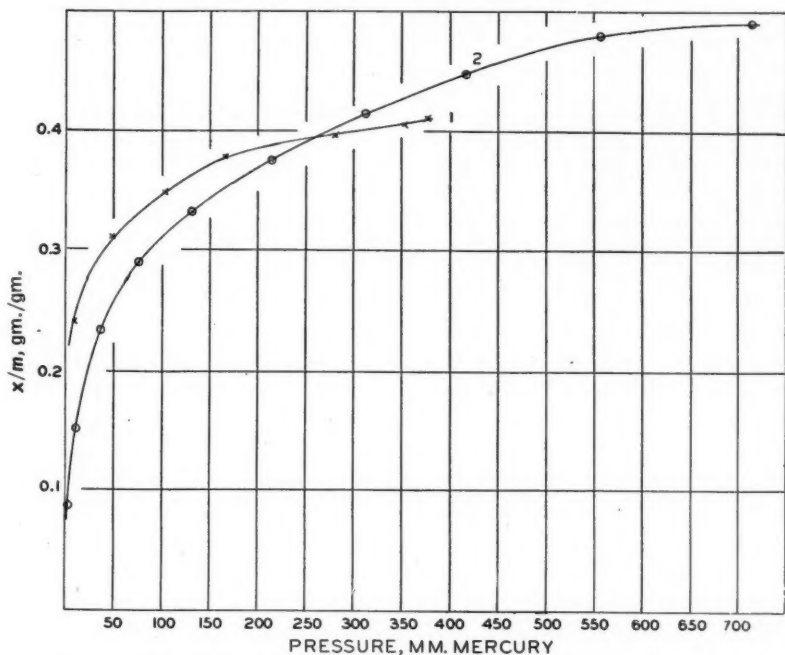


FIG. 6. Adsorption isotherms of ethyl chloride and diethyl ether on charcoal at 35° C.

Curve 1: diethyl ether.

Curve 2: ethyl chloride.

Because the flow of adsorbable gas at the higher pressures used is not greatly different from that predicted from the flow of a gas that is not highly adsorbed, it would seem that the greater part of the gas in this pressure region is passing through the charcoal by a mechanism similar to that prevailing when a permanent gas passes through the rod at corresponding pressures. If we assume that the adsorbed gas is condensed into void regions of the charcoal that do not contribute materially to the flow path, and that this condensation does not alter the structure of the charcoal as determined by the constants  $A$  and  $B$  of Equation (2), we would then be able to state that the mechanism of transport of the condensable and noncondensable gases is essentially the same. Such a situation might exist if most of the flow were through relatively large fissures. While such an explanation would be consistent with our data at the



higher pressures, it would obviously fail to account for the very considerable increase in flow rate of the condensable gases at the lower pressures. It is to be emphasized that most of the factors readily visualized, such as blocking of capillaries, relative contribution of molecular streaming, etc., should make the deviation from the Adzumi equation less at the lower pressures.

Since the increased flow rate is apparent only with the adsorbed gases, it would seem reasonable to conclude that this increase is the result of a surface phenomenon. If we accept the Maxwell (11) picture for the flow through a capillary, we might explain the phenomenon as an increase in the 'slip'. It is reasonable to suppose that if for some reason the density of a fluid flowing through a capillary were very much greater in the immediate neighborhood of the capillary wall, the contribution of the slip term would become more important than in the case of a gas whose density does not vary in this manner. If 'surface flow' or flow of adsorbed material contributes appreciably to the total flow, we would expect that there should be a relation between the adsorption isotherm and the surface flow. For a constant pressure difference the value of the mean pressure will determine the quantity of material adsorbed as well as the difference in the quantities adsorbed at the two ends of the carbon rod. The isotherms of diethyl ether and ethyl chloride (Fig. 6) show that for a constant pressure difference, the difference in the quantities adsorbed at the two ends of a charcoal rod is much more marked at low mean pressures than is this difference at high mean pressures (cf. slope of the isotherm). The marked surface concentration gradients that probably exist when adsorbable gases are flowing through a charcoal rod at low mean pressures suggests that possibly an explanation for our results is to be found in a rapid surface diffusion phenomenon.

Finally, attention is again directed to the relative values of the intercepts obtained by extrapolating our data to the flow axis. The ethyl chloride and diethyl ether intercepts are both much greater than the nitrogen intercept. Obviously, in these cases, the intercepts are not, even approximately, inversely proportional to the square roots of the molecular weights.

#### Acknowledgments

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## ABSORPTION DE L'ANHYDRIDE CARBONIQUE PAR L'ACIDE OLÉIQUE ET LE STÉARATE D'ÉTHYLE<sup>1</sup>

PAR CYRIAS OUELLET ET JEAN-T. DUBOIS

### Sommaire

L'absorption de l'anhydride carbonique par deux constituants des lipides, l'acide oléique et le stéarate d'éthyle, a été mesurée entre 23° et 74° C. Pour l'acide oléique, les coefficients de Bunsen sont:  $\alpha = 1.13$  à 23° C. et 0.69 à 62° C.;  $\Delta H = -2500$  cal. par mole. Pour le stéarate d'éthyle,  $\alpha = 1.15$  à 34° C. et 0.76 à 74° C.;  $\Delta H = -2100$  cal. par mole.  $\Delta H$  est constant dans l'intervalle de températures étudié.

### Introduction

Ce travail a été entrepris dans le but d'obtenir quelques données quantitatives sur l'absorption de l'anhydride carbonique par les lipides. Vu que ce phénomène est susceptible d'intervenir dans les processus biologiques qui comportent la pénétration de l'anhydride carbonique dans les tissus, il est remarquable qu'il n'ait pas été étudié davantage. D'après Seidell (4) et Markham et Kobe (2), il semble que les seules données existantes soient celles de Schmidt-Nielsen (3) et de Vibrans (5). Elles portent sur des huiles et graisses naturelles et indiquent que l'anhydride carbonique y est un peu plus soluble que dans l'eau à la température ordinaire.

Il nous a paru intéressant d'étudier l'absorption de ce gaz par un acide gras et un ester, afin de savoir dans quelle proportion chacun de ces constituants des lipides contribue à l'absorption totale. L'acide oléique et le stéarate d'éthyle se prêtent bien à de telles mesures parce qu'ils sont liquides à des températures pas trop élevées. Il est vraisemblable que leurs pouvoirs absorbants diffèrent peu de ceux des autres acides gras et esters de poids moléculaires voisins.

### Méthode Expérimentale

Les mesures ont été faites suivant une méthode manométrique, au moyen de l'appareil de la Fig. 1. L'absorption se faisait dans un ballon, *A*, placé dans un thermostat et relié au reste de l'appareil au moyen d'un tube de cuivre, *RS*, d'environ 1 mm. de diamètre interne, dont la flexibilité permettait une agitation violente. La capacité du ballon, des capillaires et du manomètre semi-capillaire, *M*, était de 173 cc. Le robinet *B* reliait l'appareil à une pompe Hyvac et à un réservoir où était emmagasiné, en présence de pentoxyde de phosphore, l'anhydride carbonique préparé par chauffage de carbonate de magnésium à 350° C. Le liquide au repos absorbait ou dégageait le gaz

<sup>1</sup> Manuscrit reçu le 24 mars 1947.

Contribution du Département de Chimie, Université Laval, Québec, P.Q.

très lentement, la pression ne variant que d'environ 1 mm. en 10 min., ce qui permettait de mesurer aisément la pression initiale. Les échanges gazeux étaient rapides durant l'agitation et aboutissaient en 10 ou 20 min. à des états d'équilibre qui n'étaient pas modifiés au bout de 24 h.

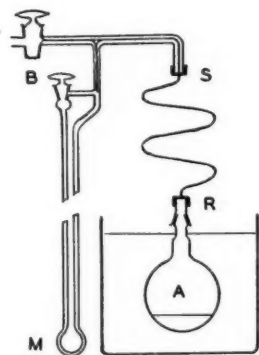


FIG. 1. Schéma de l'appareil montrant le ballon à absorption, A, le tube de cuivre flexible, RS, et le manomètre semi-capillaire, M.

Le liquide était d'abord soumis à une agitation et à une évacuation prolongées, jusqu'à ce qu'il n'en sortît plus de gaz dissous. On introduisait ensuite rapidement de l'anhydride carbonique au-dessus du liquide au repos et on lisait la pression initiale. On agitait ensuite jusqu'à ce que la pression se fût stabilisée à une nouvelle valeur. D'après l'abaissement de la pression et le volume libre du système, on calculait la quantité de gaz dissoute à la pression finale. Pour s'assurer de la réversibilité de l'absorption, on procédait aussi par désorption. Les points obtenus par ces deux méthodes tombaient invariablement sur les mêmes droites.

### Résultats

Les quantités de gaz absorbées aux diverses températures et pressions finales ont été ramenées à 0° C. et 760 mm. de mercure. Les Figs. 2 et 3 montrent les quantités absorbées par 25 cc. d'acide oléique et 25 cc. de stéarate d'éthyle. On voit que l'absorption obéit à la loi de Henry dans l'intervalle de pressions étudié et est une fonction décroissante de la température.

En exprimant les valeurs obtenues en centimètres cubes (à 0° C. et 760 mm. de mercure) de gaz absorbés par 1 cc. de liquide, sous une pression de 760 mm. de mercure on obtient les *coefficients de Bunsen*,  $\alpha$ , consignés dans le Tableau I. Les valeurs  $25\alpha$  de ce coefficient, pour 25 cc. de liquide, sont indiquées à droite des Figs. 2 et 3. Les concentrations des solutions sont aussi données, dans le tableau, en fractions de mole,  $N_2$ , d'anhydride carbonique. Pour

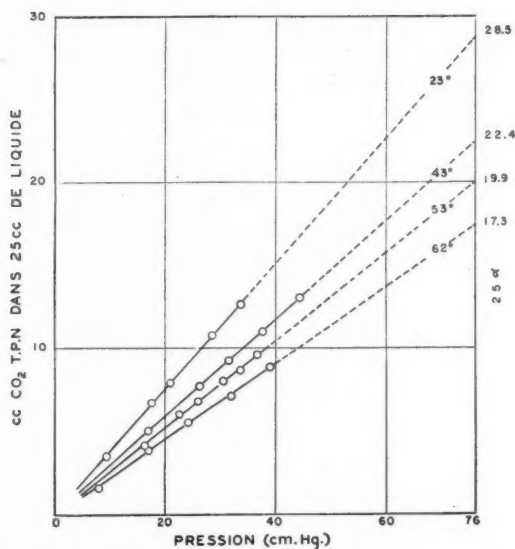


FIG. 2. Absorption de l'anhydride carbonique en centimètres cubes T.P.N. dans 25 cc. d'acide oléique.

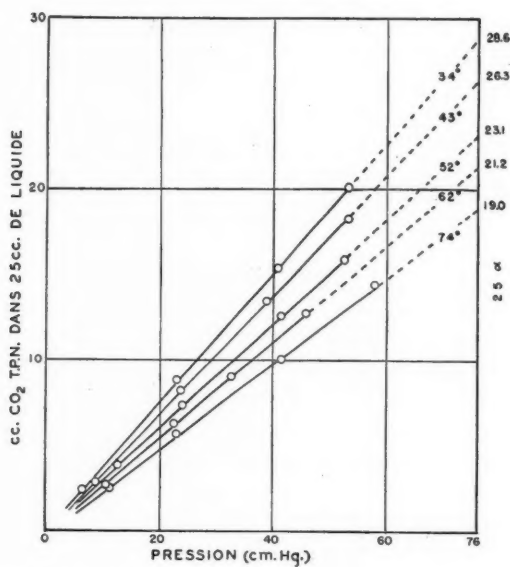


FIG. 3. Absorption de l'anhydride carbonique en centimètres cubes T.P.N. dans 25 cc. de stéarate d'éthyle.

TABLEAU I

COEFFICIENTS DE BUNSEN,  $\alpha$ , ET FRACTIONS DE MOLE,  $N_2$ , DE L'ANHYDRIDE CARBONIQUE À DIVERSES TEMPÉRATURES

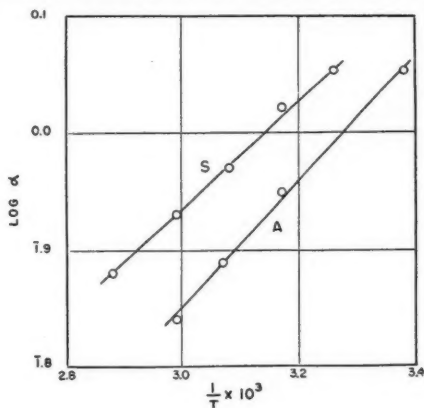
Acide oléique			Stéarate d'éthyle		
$t, ^\circ\text{C.}$	$\alpha$	$N_2$	$t, ^\circ\text{C.}$	$\alpha$	$N_2$
23.0	1.13	$1.60 \times 10^{-2}$	34.0	1.15	$1.90 \times 10^{-2}$
43.0	0.90	"	43.0	1.05	1.73 "
53.0	0.79	1.12 "	52.0	0.94	1.55 "
62.0	0.69	0.98 "	62.0	0.85	1.40 "
			74.0	0.76	1.25 "
$\Delta H = -2500 \text{ cal./mole}$			$\Delta H = -2100 \text{ cal./mole}$		

calculer ces fractions de mole, il a fallu déterminer la densité du stéarate d'éthyle. Elle est de 0.848 g. par cc. à  $40^\circ\text{C.}$

Si l'on porte en abscisses les inverses des températures absolues et en ordonnées les logarithmes des coefficients de Bunsen, on obtient les droites de la Fig. 4. Les pentes de ces droites, aussi bien que l'équation

$$\ln \frac{\alpha_2}{\alpha_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right),$$

permettent de calculer les chaleurs de dissolution  $\Delta H$  à partir des coefficients  $\alpha_1$  et  $\alpha_2$  correspondant aux températures absolues,  $T_1$  et  $T_2$ . Les valeurs de

FIG. 4. Courbes de  $\log \alpha$  contre  $1/T$  pour l'acide oléique (A) et le stéarate d'éthyle (S).

$\Delta H$  ainsi calculées se trouvent au bas du Tableau I. Comme le montrent les droites de la Fig. 4, les valeurs de  $\Delta H$  sont sensiblement constantes dans l'intervalle de températures étudié.

### Discussion

Les solubilités de l'anhydride carbonique dans cet acide gras et cet ester, ainsi que les chaleurs de dissolution, sont du même ordre de grandeur. Si l'on compare les résultats ci-dessus à ceux de Kunerth (1), on voit que l'anhydride carbonique est un peu plus soluble dans les lipides étudiés que dans l'eau, où  $\alpha = 0.90$  à  $20^\circ \text{C.}$ , mais beaucoup moins soluble que dans plusieurs liquides organiques de poids moléculaires peu élevés, parmi lesquels les valeurs de  $\alpha$  à  $20^\circ \text{C.}$  vont de 3.57 pour l'alcool méthylique à 6.98 pour l'acétone. L'analyse des résultats de Kunerth montre aussi que, pour ces liquides, la chaleur de dissolution varie rapidement avec la température; les valeurs moyennes calculées de  $\Delta H$  entre  $20^\circ$  et  $34^\circ \text{C.}$  sont de  $-2500 \text{ cal.}$  par mole pour l'alcool méthylique et de  $-5200 \text{ cal.}$  par mole pour l'acétone. Nos systèmes diffèrent donc de ces derniers surtout par les valeurs plus petites de  $\alpha$  et la constance de  $\Delta H$ .

Il est intéressant de noter que la solubilité dans l'acide oléique passe par la valeur idéale au voisinage de  $23^\circ \text{C.}$  La pression de vapeur de l'anhydride carbonique à cette température étant de  $60.7 \text{ atm.}$ , une solution idéale de ce gaz aurait une pression de vapeur de 1 atmosphère si la fraction de mole du gaz dissous était de  $1/60.7 = 1.65 \times 10^{-2}$ . L'expérience donne  $1.60 \times 10^{-2}$ . Bien que les solutions étudiées ici ne soient pas idéales, on peut retenir que les solubilités sont de l'ordre de grandeur de la solubilité idéale aux températures ordinaires.

### Remerciements

L'Office des Recherches scientifiques et industrielles de la Province de Québec a accordé une subvention à l'un des auteurs (J.-T.D.) pour ce travail de recherche.

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## A PHOTOELECTRIC STUDY OF THE RATE OF GELATINIZATION OF NITROCELLULOSE IN NITROGLYCERINE<sup>1</sup>

BY DAVID FENSOM<sup>2</sup>

### Abstract

The process of gelatinization of nitrocellulose in a mixed solvent consisting of 80% glyceryl trinitrate and 20% ethylene glycol dinitrate by weight has been followed by using a commercial electrophotometer. The light scattered and absorbed by the colloid in its solvent was found to be dependent on the amount of nitrocellulose undissolved by the solvent at any time. The rate of gelatinization and the presence of insoluble fibers were related to the method of nitration and to the treatment of the raw material for nitrocellulose.

Measurements on the rate or degree of gelatinization of high polymers in solution have been made by a number of investigators (5, 6, 10) and the same methods have been used with more or less success in the case of nitrocellulose. The change in viscosity of nitrocellulose-nitroglycerine gels (3, 9) has provided some information on this particular system, but it appears that there is no published account of the use of light-scattering methods (7, 10) to investigate the formation of gels from these materials. The measurements with the electrophotometer, described below, were adapted for industrial purposes, but it is believed that the results may be of general scientific interest.

### Experimental

A standard Fisher Electrophotometer, with a green filter No. B. 525 across the light beam, was used for this work. The instrument contained a comparator photoelectric cell, and all readings of light absorption in solutions were referred to a standard sample of the filtered solvent. This apparatus measured the light passing through the test solutions in a very convenient manner, but it did not assess the light scattering properties of the colloid alone (7, 8). Solutions were made up and tested in the cylindrical glass test tubes that were supplied with the meter.

The nitrocellulose samples used were obtained from normal manufacture without special purification or fractionation. They were broken down in the water-wet state by passing them eight times through a Wiley mill running at 1725 r.p.m., followed by drying at 70° C. As a result of this treatment, different samples did not have identical particle size, but the fibers were well broken up and were generally sufficiently uniform in size range to allow a comparison of their behavior to be made. A wide variety of grades of nitrocellulose was used.

<sup>1</sup> Manuscript received in original form July 8, 1947, and, as revised, September 10, 1947.

Contribution from Canadian Armament Research Establishment, P.O. Box 1427, Quebec, Que.

<sup>2</sup> Present address: Ridley College, St. Catharines, Ont.

The solvent used throughout this work was a mixture of 80% glyceryl trinitrate and 20% ethylene glycol dinitrate, by weight. This material was filtered and used because of its excellent solvent range for nitrocelluloses of different nitrogen contents, and because other work (3, 4) had been carried out on the same materials.

In the standard procedure, 0.400 gm. of the dry powdered nitrocellulose was shaken on to the surface of the nitroglycerine at 'zero' time. The powder was immediately stirred underneath the surface of the liquid and incorporated evenly throughout it. Thirty seconds was allowed for the addition and 30 sec. for the stirring. The 'log of light absorption' scale was read on the photometer 60 sec. from zero time and at progressively longer intervals as gelatinization proceeded. The solution was stirred for 30 sec. before each reading was taken, but not between readings. Some sedimentation occurred when the sample remained overnight and swelling was not sufficient to make settling very slow. All work was done between 22° to 25° C. in 20.0 ml. of solvent.

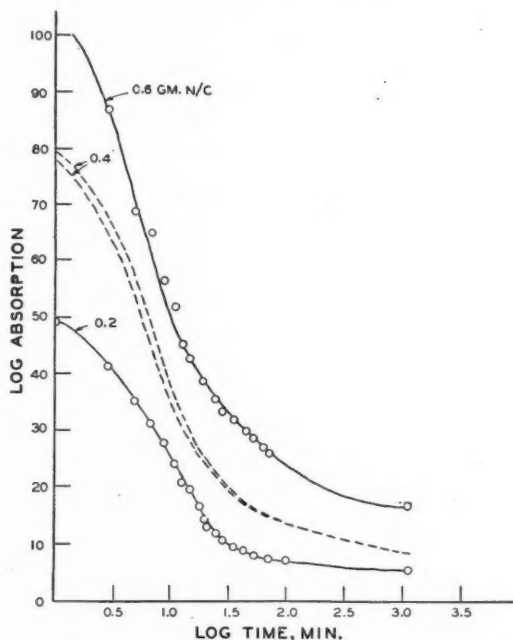


FIG. 1. Different concentrations of N/C 19 in C nitroglycerine.

As the results were obtained, the log absorption as read by the photometer scale was plotted against the log of time. An example of the variation in results from two different samples of the same nitrocellulose is shown in Fig. 1.

TABLE I

RATES OF GELATINIZATION AND RESIDUAL UNGELATINIZED MATERIAL OF SOLUTIONS OF NITROCELLULOSE IN NITROGLYCERINE<sup>1</sup>

Nitrocellulose Reference No.	Nitrocellulose trade name	Rate of gelatinization, log absorption log time	Residual material after three days, log absorption
13	AS $\frac{1}{2}$ sec.	2.4	76
12	AS $\frac{1}{2}$ sec.	-5	100
36	Low soluble	2.6	55
30	LL 55	10	44
19	RS $\frac{1}{4}$ sec	54	7.0
11	RS $\frac{1}{4}$ sec	54	12
6	—	29	8.0
37	HX 8-13	54	5.0
32	HX 8-13	57	9.0
3	RS 15-20	40	12
8	—	39	16
38	HL 120-170	53	7.5
34	HM 15-20	34	6.5
2	RS 70	28	15
9	—	31	19
31	HH 5-15	41	12
33	Blasting N/C	52	36
5	" "	50	32
28	—	18	34
24	—	24	29
1	Propulsive soluble N/C	21	50
35	Pyro N/C	22	24
20	—	25	20
14	—	9.0	50
21	—	13	70
26	—	6.0	80
25	—	9.6	80
39	—	5.8	42
23	—	7.8	72
22	—	6.6	72

<sup>1</sup> The nitroglycerine solvent (referred to in the captions to the figures as C nitroglycerine) was 80 : 20 nitroglycerine-nitroglycol mixture. This table refers to 0.400 gm. N/C in 20 ml. solvent.

For the sake of brevity the complete experimental results for samples of nitrocellulose are shown only in Figs. 1 to 7 inclusive. The characteristics of all samples examined, including those given in the figures, are summarized in Table I in groups of rising nitrogen content. In this table the rate of gelatinization was measured by the slope of the steep part of the gelatinization curve (e.g., from Figs. 1 to 7), and the residual material was measured from the figures by the log absorption reading at the three-day period. The basic properties of these samples are given in Table II.

TABLE II  
PROPERTIES OF NITROCELLULOSES USED IN PRESENT WORK

Nitrocellulose Reference No.	Raw material	Industrial nitration process	Nitrogen, %	Intrinsic viscosity in <i>n</i> -butyl acetate, [ $\eta$ ]
13	Cotton linters	Mechanical	10.65	0.54
12	" "	"	10.62	2.48
36	" "	Displacement	10.89	3.63
30	" "	Mechanical	11.36	2.76
19	" "	"	11.63	0.68
11	" "	"	11.71	0.80
6	Viscose flakes	"	11.86	0.90
37	Cotton linters	"	12.03	0.93
32	" "	"	11.96	1.07
3	" "	"	11.75	1.50
8	" "	"	11.79	1.69
38	" "	"	12.02	2.17
34	" "	"	12.15	2.49
2	" "	"	11.94	3.07
9	" "	"	12.07	4.45
31	" "	"	12.23	5.90
33	" cops	Ardeer	11.99	7.12
5	" linters	Mechanical	12.28	10.6
28	" "	Displacement	12.24	2.51
24	Wood pulp	"	12.17	3.43
1	" "	"	12.28	3.75
35	Cotton linters	Mechanical	12.63	3.05
20	Wood pulp	"	12.58	3.51
14	" "	Displacement	13.01	4.27
21	" "	"	13.02	4.73
26	" "	"	13.16	4.79
25	" "	"	13.01	5.95
39	Cotton linters	Mechanical	13.42	3.23
23	Wood pulp	"	13.39	3.46
22	" "	"	13.43	3.61

### Discussion of Results

The exact meaning of the curves of light absorption obtained in the manner described is difficult to establish quantitatively. Included in the light absorbed by the colloid solutions as obtained by the photometer was light screened out by the particles, light scattered by particles according to the Tyndall effect, and light absorbed by the true solution according to Beer's law. Dognon (1) and Krishnamurti (2, 8) have discussed the various factors pertaining to light transmission or light scattering through dispersions, but because of the simplified procedure no attempt has been made to express the results of this

work in terms of their equations. Dognon, however, has pointed out that if the particle size is above  $0.5 \mu$ , a condition pertaining to the solutions tested, flocculation or other increase in size of some particles (total weight of particles remaining the same) will be accompanied by a decrease in absorption according to the relation

$$\log \frac{I_0}{I} \propto \frac{1}{r}, \quad (a)$$

but if the number of particles remains the same when the size is decreasing, the absorption will decrease according to the relation

$$\log \frac{I_0}{I} \propto r^2, \quad (b)$$

where  $I_0$  is the intensity of incident light (as measured by the comparator cell),  $I$  is the intensity of total transmitted light (as measured by the receptor cell), and  $r$  is the radius of a spherical particle.

In the photometer used throughout this work,  $\log \frac{I_0}{I}$  was read directly from a scale as 'log absorption', and this is the term dealt with by Relations (a) and (b). Therefore a decrease in log absorption of light through a dispersion indicates one or a combination of three conditions; (i) that the suspended particles are more completely dispersed when the conditions pertaining to Relation (a) are dominant, (ii) that the particles are decreasing in size in the solution or are dissolving (as opposed to swelling) when the conditions pertaining to Relation (b) dominate, or (iii) that complete solution of some granules occurs, which leads to the reduction of the number of light-absorbing particles. But gelatinization involves the combined dispersion, the solution, and in some instances the swelling, of particles in a solvent; therefore it is reasonable to use the log absorption as a measure of gelatinization. The rate of gelatinization may then be expressed by the slope of the log absorption curve with time, or conveniently by  $\frac{\log \text{absorption}}{\log \text{time}}$ . This relation is confirmed by experiment, since in Fig. 1 the log absorption depended on the concentration of ungelatinized colloid which obviously decreased as time progressed. The residual absorption is also of interest as a measure of the material imperfectly gelatinized which will not change in light absorbing properties over a long period of time.

In Fig. 2 the rate of gelatinization curves are shown for a number of nitrocelluloses made from cotton linters by a mechanical nitration process. It may be seen from this figure that the same shape of curve was obtained for all these samples. Since the concentrations were all the same in this series, the initial figure on the log absorption axis was a measure of fineness of division of nitrocellulose (1). The low viscosity nitrocellulose gave a faster rate than

the high viscosity samples, and the high viscosity sample (whose nitrogen content was also higher than the others) gave residual material considerably in excess of that of the others. Several units of this were probably due to the

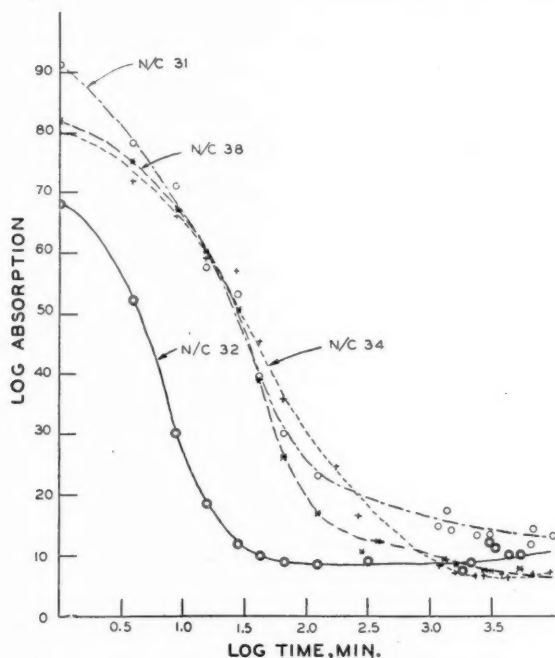


FIG. 2. Different viscosities of soluble nitrocellulose in C nitroglycerine. N/C 31,  $[\eta] = 5.90$ ; N/C 34,  $[\eta] = 2.49$ ; N/C 38,  $[\eta] = 2.17$ ; N/C 32,  $[\eta] = 1.07$ .

increase in light absorption of the solution over the light absorption of the solvent according to Beer's law, but some suspended matter was clearly visible and in several cases the residual solution was centrifuged, the supernatant liquid decanted, and the residue washed with fresh solvent and again centrifuged. Final washings were done with ether and the residue dried at  $70^{\circ}\text{C}$ . A microscopical examination of this residue with the aid of crystal violet base dye in nitroglycerine (4) showed that the material consisted of fiber shreds and of short fibers of nitrogen content 11.0 to 11.5% in fiber skins which were resistant to solution.

Fig. 3 illustrates the difference between the solubility rates of two nitrocelluloses nitrated from linters to the same nitrogen value, without viscosity reduction, by two different methods. In this case the sample nitrated mechanically (N/C 31) had a much faster rate of gelatinization and also had much less light absorbing residue after gelatinization had ceased. This indicated

that the product from mechanical nitration was much more uniform in solubility and nitrogen content than was material made by the displacement process.

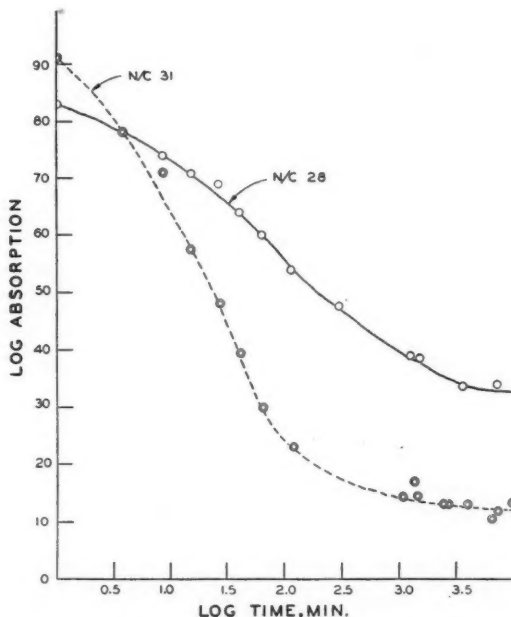


FIG. 3. Nitrocellulose of different methods of nitration in *C* nitroglycerine. N/C 31, mechanical; N/C 28, displacement; both 12.2% N.

The differences in gelatinization rates that can be expected from changing the raw material in displacement nitration are shown in Fig. 4. In this case it may be seen that N/C 1 (made from tissue paper) had a curve similar in form to that of N/C 28 (from cotton linters), while the curve of N/C 24 (from wood-pulp) was rather different in shape. It can be seen that, of these samples, N/C 1 had considerably more residual material left and, from a microscopical examination, it appeared that this material was the least uniform in nitrogen content of its individual fibers. The residual fibers in this case tended to have a nitrogen content above 12.5%. The sample N/C 33 was made from cotton cops and was nitrated by a type of displacement process that tended to produce a less uniform product. This material had a very fast rate of gelatinization and also a substantial fraction of light absorbent material left over. The residual material in this case was found to contain fibers of both a low and a high nitrogen range.

The differences in gelatinization caused by different raw materials are shown even more markedly by Fig. 5. In this figure the curves of N/C 19 and N/C 11 (both from cotton linters) have been plotted together with the



curve of N/C 6 (from viscose chips). The viscose nitrocellulose was coarser, as is shown by the low initial absorption, but it was also much slower in gelatinizing.

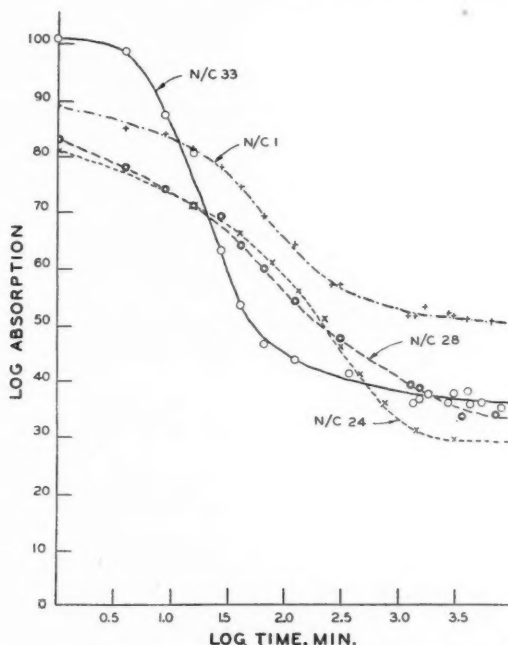


FIG. 4. Nitrocellulose from different raw materials in C nitroglycerine. N/C 1, wood-pulp; N/C 24, wood-pulp; N/C 28, linters; N/C 33, cotton cops; 12.2% N.

In Fig. 6 the curves of three nitrocelluloses are shown. In each case the sample was taken without treatment to break down the fibers, and the gelatinization rate was measured (*a* curves). The samples were then milled as described in the procedure, and the new rates were measured (*b* curves).

In Fig. 7 the curves for five samples are shown. In each case the raw material was cotton linters and the nitration was by the mechanical method. These samples were untreated for viscosity reduction, but the nitrogen content varied from 10.6 to 13.4%. The gelatinization curves showed very clearly that the lower nitrogen material was relatively insoluble in the mixed nitroglycerine solvent at room temperature, the solubility becoming appreciable only with nitrocellulose containing more than 11.4% N. The least residue was obtained with 12.2% nitrogen material, and with higher nitrogen content the nitrocellulose became increasingly less soluble. The rates of gelatinization followed closely the order of solubility of the samples.

The mixed nitric ester solvent used in this study, as Table I shows, did not appreciably dissolve nitrocellulose fibers of nitrogen content 13.0% or

above, nor below 11.0%. In some cases fibers with an intermediate nitrogen content did not dissolve, possibly because of the presence of films of less soluble material on the outside of the fibers. The residual material, as shown up by

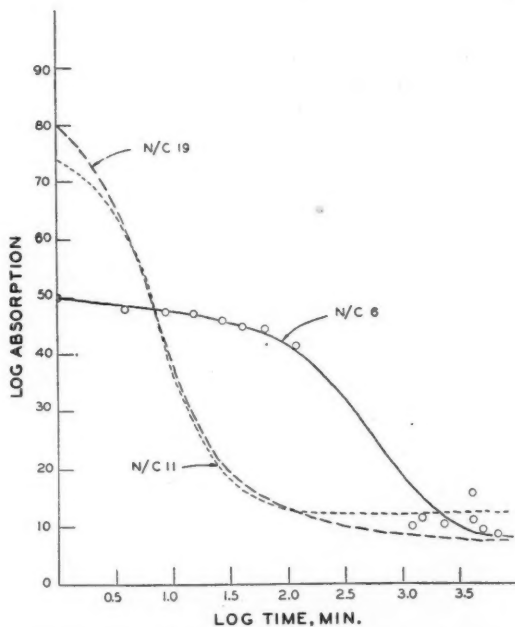


FIG. 5. Nitrocellulose from different raw materials in C nitroglycerine. N/C 6, viscose flakes; N/C 11, linters; N/C 19, linters; 11.7 % N.

the residual absorption, was a measure of both high-nitrated and low-nitrated fibers, and, where the average nitrogen content lay within the soluble range, it thus measured the uniformity of the total material.

It has been shown above that mechanically nitrated material was much more uniform in the solubility and nitrogen content of its fibers than was material nitrated by the displacement process. This suggests that the lack of homogeneity achieved in the displacement process is probably caused by the zone of diluted acid passing down through the bulk of the material as the strong acid is displaced with water, since it is known that the temperature rises in this zone and the time would be long enough for denitration to occur in some fibers, at least.

### Conclusion

The photoelectric method of following the gelatinization of nitrocellulose in a mixed nitroglycerine-nitroglycol solvent has been found to be useful for examining the properties of different nitrocelluloses and the mechanism of gelatinization.

A qualitative relation has been found between the logarithm of the light absorbed and scattered by the suspensions and the concentration of ungelatinized material.

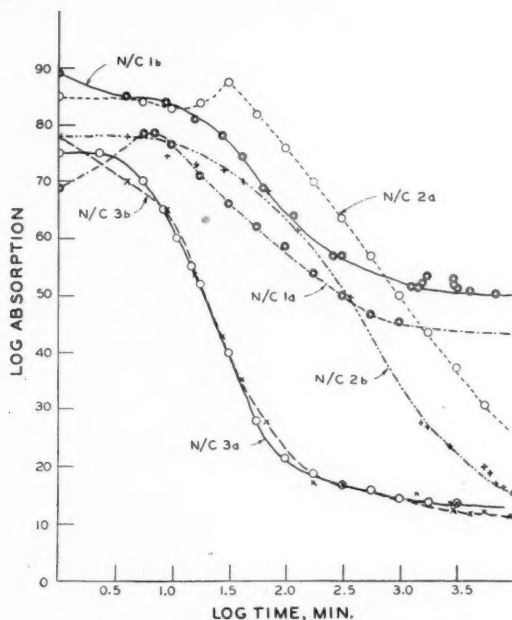


FIG. 6. Nitrocellulose in *C* nitroglycerine. Preparation: a curves, from milled samples. b curves, from unmilled samples.

The residual light absorption was found to be a measure of the low-nitrated plus high-nitrated material ungelled by the mixed solvent.

Displacement nitration was again found to give a much less uniform product than mechanical nitration, and with greater quantities of insoluble residual material.

In addition to the distribution of insoluble material shown up by this photoelectric method, it has been shown that it is possible to compare rates of gelatinization. The rate of gelatinization has been found to vary with a number of factors. It varied with the nitrogen content, although the precise relation was masked by any film effect that might be connected with the fibers. It varied with viscosity, though again this effect could be hidden by the much more important factor of the way in which the fibers were broken up. This break-up of fibers, which includes on the one hand the fineness of the material and on the other the amount of disturbance to the fiber skin, is undoubtedly one of the most important factors (4). Since many industrial nitrocelluloses are blends of material of different viscosity, the rate of gelatinization curves also show different slopes throughout their length, indicative

of the blending. Finally, in those anomalous cases where the curve of gelatinization was markedly different from the regular curves, it has been suggested that the explanation lies in a factor resulting from the treatment of the raw material before nitration, such as the drying of the cellulose.

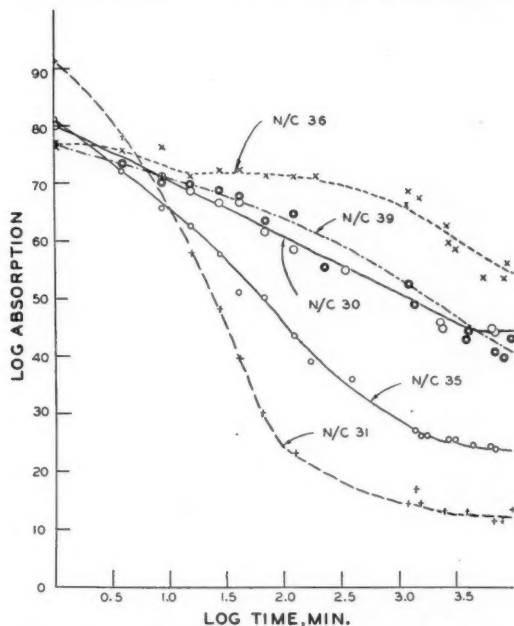


FIG. 7. Nitrocellulose of different nitrogen content in C nitroglycerine. Nitrocellulose obtained by mechanical nitration of cotton linters. N/C 30, 11.4% N; N/C 31, 12.2% N; N/C 35, 12.6% N; N/C 36, 10.9% N; N/C 39, 13.4% N.

### Acknowledgments

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## APPLICATION DE LA RÉACTION DE MEERWEIN À LA SYNTHÈSE DE DÉRIVÉS DISUBSTITUÉS DU STILBÈNE<sup>1</sup>

PAR P. L'ECUYER, F. TURCOTTE, J. GIGUÈRE, C. A. OLIVIER ET P. ROBFRGE

### Sommaire

En faisant réagir la solution aqueuse des sels de diazonium monosubstitués avec des solutions d'acides cinnamiques substitués selon les conditions publiées par Meerwein, il a été possible de synthétiser un certain nombre de dérivés du stilbène avec un groupement substituant dans chacun des anneaux benzéniques. De cette façon ont été synthétisés pour la première fois les composés suivants: 4-bromo-4'-nitrostilbène, 2-chloro-4'-bromostilbène, 2-chloro-2'-méthoxystilbène, 2-chloro-4'-phénylstilbène, 2-chloro-2'-nitrostilbène, 2-chloro-3'-nitrostilbène, 2-chloro-4'-nitrostilbène, 4-chloro-4'-nitrostilbène, 2,2'-dichlorostilbène, 2,4'-dichlorostilbène, 2-méthoxy-4'-bromostilbène, 2-méthoxy-4'-chlorostilbène, 2-méthoxy-2'-nitrostilbène, 2-méthoxy-3'-nitrostilbène, 2-méthoxy-4'-phénylstilbène, 3-nitro-4'-bromostilbène, 3-nitro-4'-chlorostilbène, 3-nitro-2'-méthylstilbène, 3-nitro-4'-méthylstilbène, 3-nitro-4'-méthoxystilbène et 4-nitro-4'-phénylstilbène. Par cette méthode ont aussi été préparés les composés suivants dont la synthèse selon une autre méthode a déjà été rapportée: 2-chloro-4'-méthoxystilbène, 2,2'-diméthoxystilbène, 2,4'-diméthoxystilbène, 4,4'-dinitrostilbène, 4-méthyl-4'-nitrostilbène, 2-méthoxy-4'-nitrostilbène et 4-méthoxy-4'-nitrostilbène.

### Introduction

La condensation des sels de diazonium aromatiques et des acides cinnamiques (15) conduit à la formation de dérivés, en vertu de l'attachement du radical aryle du sel de diazonium au carbone  $\alpha$  de l'acide, suivi de l'élimination spontanée d'azote et d'anhydride carbonique. Les auteurs (2, 3, 4, 5, 13) qui ont appliqué cette méthode de synthèse à la suite de Meerwein se sont, en général, limités à l'étude du comportement des divers sels diazonium avec l'acide cinnamique, obtenant des dérivés unilatéralement substitués.

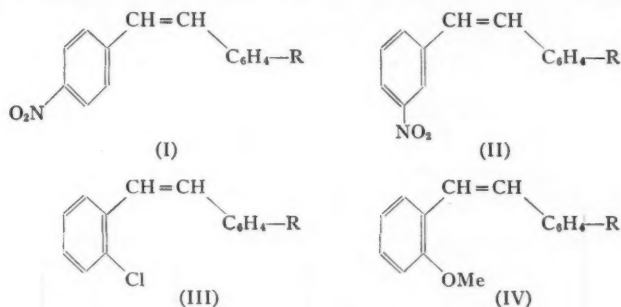
Le présent travail rapporte la synthèse de dérivés du stilbène possédant des groupements substituants dans les deux anneaux benzéniques, grâce à l'emploi d'acides cinnamiques substitués, notamment les acides *o*-chlorocinnamique, *o*-méthoxycinnamique, *m*- et *p*-nitrocinnamiques. Deux des auteurs (L'Ecuyer et Turcotte) avaient auparavant appliqué avec succès cette méthode de synthèse à l'acide *m*-nitrocinnamique, dans le but d'obtenir des stilbènes dinitrés.

Dans leur application originale (15) Meerwein et ses collaborateurs recommandent l'emploi exclusif de l'acétone comme solvant des composés qui subissent la réaction avec les sels diazonium, les autres solvants miscibles à l'eau, notamment l'alcool et le dioxane, ne permettant pas le mécanisme qui fait l'essence de la réaction. Il en résulte que la solubilité très variable des acides cinnamiques substitués dans ce solvant nous empêche d'opérer dans des conditions de milieu absolument identiques. C'est sans doute pour cette

<sup>1</sup> Manuscrit reçu le 17 septembre 1947.

Contribution du Département de Chimie de la Faculté des Sciences, Université Laval, Québec.

raison qu'il nous semble impossible, actuellement, de relier la réactivité de ces acides suivant la position des groupements substituants d'une façon aussi simple que Bergmann l'a fait pour les sels de diazonium (5). Nous constatons,



R = Cl, Br, CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, OCH<sub>3</sub> ou NO<sub>2</sub> en position *o*-, *m*- ou *p*-.

par exemple, que l'acide *p*-méthoxycinnamique a fourni à Meerwein des rendements supérieurs à ceux que nous obtenons avec son isomère *ortho*-, tandis que l'acide *o*-chlorocinnamique est nettement supérieur à son isomère *para*- sous ce rapport. Le volume d'acétone relativement énorme qui est nécessaire pour dissoudre l'acide *p*-nitrocinnamique affecte le rendement à un point tel que Meerwein lui-même ne discerna pas de traces de réaction (15). Les résultats que nous obtenons le situent, dans presque tous les cas, après son isomère *méto*-, qui est un peu plus soluble.

Les quatre acides cinnamiques substitués ainsi employés furent soumis à l'action des solutions aqueuses des sels de diazonium correspondant aux amines suivantes: *o*- et *p*-chloranilines, *p*-bromaniline, *o*-, *m*- et *p*-nitranilines, *p*-aminodiphényle, *p*-toluidine et *p*-anisidine.

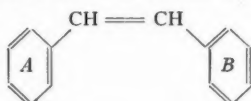
Dans certains cas nous parvenons au même dérivé disubstitué en partant de produits inversement substitués. Il est intéressant de noter, par exemple, que pour la synthèse des stilbènes orthochlorés le rendement est généralement supérieur lorsque l'atome de chlore est fixé à l'acide cinnamique, en raison de la répugnance relative des amines orthosubstituées à subir la réaction de Meerwein (5). C'est ce qui ressort de la préparation des 2-chloro-3'-nitro- et 2-chloro-4'-nitrostilbènes par les deux voies possibles. La même constatation s'applique également à la synthèse du 2-méthoxy-3'-nitrostilbène par les deux procédés possibles. Dans tous les cas nous avons vérifié l'identité, d'ailleurs évidente, de ces composés au moyen de points de fusion mixtes.

Certains composés que nous avons préparés l'avaient été auparavant par d'autres méthodes, principalement par la réaction de Perkin. Dans tous les cas rapportés ici, nous croyons à la coïncidence de nos résultats, les points de fusion étant presque toujours en accord avec les données antérieures. Les faibles écarts que nous avons rencontrés en quelques occasions sont compensés par la concordance des résultats de l'analyse quantitative.

Dans le Tableau I des points de fusion que nous avons dressé, nous indiquons les deux points de fusion avec la référence à la littérature, s'il y a lieu. Ce tableau montre que les points de fusion des stilbènes disubstitués en position

TABLEAU I

POINTS DE FUSION EN RAPPORT AVEC LA POSITION DES GROUPEMENTS SUBSTITUANTS



Substituant en A	Substituant en B				
	H	<i>o</i> -Cl	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>	<i>o</i> -OCH <sub>3</sub>
<i>o</i> -Cl	39-40° (10)	97° (7)	108°	123°	—
<i>p</i> -Cl	129° (14, 24)	71°	122-123°	186-187°	83-84°
<i>o</i> -NO <sub>2</sub>	72° (18, 22)	110-111	150° (13)	140° (20) 143°	81-82°
<i>m</i> -NO <sub>2</sub>	112° (13)	108°	242° (13)	220° (13)	89°
<i>p</i> -NO <sub>2</sub>	155° (19)	125°	220° (13)	294° (8)	120° 122° (16)
<i>p</i> -CH <sub>3</sub>	117° (14) 120° (15)	42-43°	99°	150° (16) 153°	186-187°
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	209° (4) 221° (12)	135°	—	216-218°	184-185°
<i>o</i> -OCH <sub>3</sub>	68° (9, 13) 70° (6)	—	86-88°	120° 122° (16)	136° (11)
<i>p</i> -OCH <sub>3</sub>	136° (23)	62-63° (13)	91°	132° (16)	95° (21)
<i>p</i> -Br	139° (1, 5)	85-86°	118°	201°	88°
<i>o</i> -CH <sub>3</sub>	—	—	86°	—	—

2,2'-, c'est-à-dire symétriques, si l'on peut dire, quant à la position sinon quant à la nature du substituant, sont plus élevés que ne permettrait de prévoir la gradation classique *o*-<*m*-<*p*- à laquelle les stilbènes mono-substitués obéissent fidèlement. Ainsi le 2,2'-dichlorostilbène, entièrement symétrique, fond à plus haute température que son isomère, 2,4'-; il en va de même des 2,2'-diméthoxy- et 2,2'-dinitrostilbènes comparés à leurs isomères 2,4'-. Ce qui semble encore plus surprenant, c'est la constatation que le 2-chloro-2'-nitrostilbène possède un point de fusion légèrement supérieur à son isomère 2-chloro-3'-nitrostilbène.

Quant au travail expérimental, nous avons opéré la diazotation des amines selon les conditions suggérées par Meerwein (15), en employant de l'acide chlorhydrique à 25%; et, à l'instar de Bergmann (2, 3, 4, 5), nous avons fréquemment omis l'extraction au benzène appliquée au résidu de la distillation



à la vapeur d'eau qui suit la réaction. A ce point, en effet, il est généralement possible d'isoler directement le produit de la réaction par trituration avec un solvant tel que l'acide acétique ou par distillation ou sublimation dans un vide de l'ordre de 0.001 mm. de mercure.

Sauf dans le cas de l'*o*-anisidine, la réaction s'effectue avec succès à des températures variant de 15° à 25° C., la chaleur dégagée pendant la réaction suffisant, en général, à élever la température du mélange réactionnel. Quant à la quantité d'acétone à employer comme solvant, elle est définie par la solubilité du composé carbonyle et il semble que la seule règle à suivre soit d'employer la quantité suffisante pour retenir l'acide en solution après sa mise en solution à chaud et refroidissement à 0° C.

Toutes nos expériences ont été conduites avec une fraction de mole égale d'amine diazotée et d'acide. Nos rendements ont été calculés en fonction de l'amine employée. La possibilité de récupérer en partie l'acide cinnamique non utilisé par neutralisation des eaux ammoniacales augmente le rendement efficace d'une façon appréciable.

### Partie expérimentale

#### 4-Chloro-4'-nitrostilbène (*I*, *R* = *p*-chloro)

Un mélange de *p*-chloraniline (12.8 g., 0.1 mole), d'acide chlorhydrique à 25% (50 ml.) et de glace (50 g.) maintenu à une température inférieure à 5° C. est diazoté par l'addition graduelle d'une solution de nitrite de sodium (8.4 g.) dans l'eau (16 ml.). Le chlorure de *p*-chlorobenzènediazonium ainsi formé est versé dans un mélange refroidi d'acide *p*-nitrocinnamique (19.3 g., 0.1 mole) dissous dans l'acétone (2000 ml.) et d'acétate de sodium anhydre (25 g.). L'addition d'une solution de chlorure de cuivre dihydraté (4.2 g.) dans l'eau (12 ml.) catalyse la réaction qui commence vers 5° C. et se caractérise par un dégagement d'azote et d'anhydride carbonique et une élévation de température qui atteint 12° C. Après trois heures d'agitation mécanique le dégagement gazeux est fini et la réaction terminée. L'acétone est alors chassée par la distillation à la vapeur d'eau en même temps que les produits secondaires volatils de la réaction, et le résidu, après la décantation de la liqueur surnageante, est lavé à l'ammoniaque 2 *N*, trituré avec de l'acide acétique, puis cristallisé du même solvant après une décoloration au noir animal. Le 4-chloro-4'-nitrostilbène se présente sous forme d'aiguilles jaune pâle de point de fusion 186° à 187° C. Rendement, 3.0 g. ou 12%. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé: N, 5.3%.

#### 2-Chloro-4'-nitrostilbène (*I*, *R* = *o*-chloro)

Le chlorure d'*o*-chlorobenzène diazonium (0.1 mole) ajouté, dans les conditions employées pour son isomère *para*-, à une solution d'acide *p*-nitrocinnamique (0.1 mole), donne naissance après trois heures d'agitation, entre 7° et 12° C., au 2-chloro-4'-nitrostilbène. Le produit de la réaction est purifié par une distillation à la vapeur d'eau. Du résidu, lavé à l'ammoniaque 2 *N*, cristallise de l'acide acétique après une décoloration au noir animal le

2-chloro-4'-nitrostilbène sous forme de fines aiguilles jaunes de point de fusion 124° à 125° C. Rendement, 1.2 g. ou 5%.

La réaction de Meerwein entre l'acide *o*-chlorocinnamique (0.1 mole) et le sel de diazonium dérivé de la *p*-nitraniline (0.1 mole) s'effectue en trois heures entre 7° et 12° C. et donne aussi le 2-chloro-4'-nitrostilbène qui est isolé de la même façon, mais avec un rendement de 6.8 g. ou 26%. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé: N, 5.3%.

*4-Méthoxy-4'-nitrostilbène (I, R = p-méthoxy) (16)*

La solution de *p*-méthoxybenzènediazonium, préparée par la diazotation de la *p*-anisidine (12.3 g., 0.1 mole) en milieu chlorhydrique, réagit avec un mélange contenant une fraction de mole équivalente d'acide *p*-nitrocinnamique, dans les mêmes conditions que pour le 4-chloro-4'-nitrostilbène. La réaction commence vers 7° C. et persiste durant trois heures à la température de 10° à 12° C. Le méthoxy-4'-nitrostilbène brut est isolé de la façon habituelle par trituration avec de l'acide acétique glacial. Il cristallise de l'alcool éthylique à 95%, après une décoloration au noir animal. Il se présente sous forme de feuillets jaunes de point de fusion 132° à 133° C. Rendement, 2.5 g. ou 10%. Calculé pour  $C_{15}H_{13}O_3N$ : N, 5.5%. Trouvé: N, 5.3%.

*2-Méthoxy-4'-nitrostilbène (I, R = o-méthoxy) (16)*

La réaction de Meerwein entre l'acide *p*-nitrocinnamique (0.1 mole) et le sel de diazonium provenant de l'*o*-anisidine (0.1 mole) débute à 8° C. et se complète à 15° C. par trois heures d'agitation mécanique. Le 2-méthoxy-4'-nitrostilbène distille à 120° à 130° C. (0.005 mm.) et cristallise de l'alcool en aiguilles jaune pâle de point de fusion 119° à 121° C. Rendement, 2.0 g. ou 8%. Calculé pour  $C_{15}H_{13}O_3N$ : N, 5.5%. Trouvé: N, 5.3%.

La réaction de Meerwein entre l'acide *o*-méthoxycinnamique (0.1 mole) et le chlorure de diazonium préparé de la *p*-nitraniline (0.1 mole) s'effectue à 8° à 15° C. et se prolonge durant trois heures. Rendement, 2.0 g. ou 8%. P.f. 119° C. P.f. mixte 119° à 120° C.

*4,4'-Dinitrostilbène (I, R = p-nitro) (8, 17)*

La solution aqueuse du chlorure de *p*-nitrobenzènediazonium préparé à partir de la *p*-nitraniline (13.8 g., 0.1 mole) est soumise à la réaction de Meerwein avec une fraction de mole égale d'acide *p*-nitrocinnamique selon les conditions mentionnées pour la préparation du 4-chloro-4'-nitrostilbène. La copulation s'effectue à 8° à 10° C. et dure trois heures. Le 4,4'-dinitrostilbène cristallise par trituration à l'acide acétique sous forme d'aiguilles jaunes de point de fusion 294° à 295° C. Rendement, 3.0 g. ou 11%. Calculé pour  $C_{14}H_{10}O_4N_2$ : N, 10.3%. Trouvé: N, 10.1%.

*2,4'-Dinitrostilbène (I, R = o-nitro) (20)*

La réaction de Meerwein entre l'acide *p*-nitrocinnamique et le sel diazonium provenant de l'*o*-nitraniline s'effectue avantageusement entre 5° et 8° C. Le 2,4'-dinitrostilbène se sublime entre 130° et 140° C. (0.001 mm.) et cristallise

de l'alcool à 95%, sous forme de lamelles jaune pâle de point de fusion 143° C. Rendement, 1.2 g. ou 5%. Calculé pour  $C_{14}H_{10}O_4N_2$ : N, 10.3%. Trouvé: N, 10.1%.

*4-Bromo-4'-nitrostilbène (I, R = p-bromo)*

La solution qui résulte de la diazotation de la *p*-bromaniline (17.2 g., 0.1 mole) est ajoutée à la solution contenant l'acide *p*-nitrocinnamique (0.1 mole). Le dégagement gazeux commence à 8° C. et persiste pendant trois heures à 12° à 15° C. Le 4-bromo-4'-nitrostilbène cristallise par trituration à l'acide acétique glacial. Recristallisé du même solvant il donne des petits prismes jaunes de point de fusion 201° C. Rendement, 2.5 g. ou 8%. Calculé pour  $C_{14}H_{10}O_2NBr$ : N, 4.6%. Trouvé: N, 4.4%.

*4-Nitro-4'-phénylstilbène (I, R = p-phényl)*

Le chlorhydrate du *p*-aminodiphényle est d'abord préparé par l'addition d'acide chlorhydrique concentré (12 ml.) à une solution bouillante de l'amine (16.9 g., 0.1 mole) dans l'éthanol (800 ml.). Il est ensuite séparé par filtration et séché, puis soumis à la diazotation de la façon habituelle. La réaction de Meerwein entre le sel de diazonium ainsi obtenu et l'acide *p*-nitrocinnamique (0.1 mole) débute, dans les conditions habituelles, vers 12° C. et se termine après quatre heures vers 20° C. Du produit de la réaction isolé de la façon ordinaire le 4-nitro-4'-phénylstilbène cristallise par trituration à l'acide acétique glacial. Recristallisé du même solvant il apparaît sous forme de prismes jaune serin de point de fusion 216° à 218° C. Rendement, 2.5 g. ou 8%. Par sublimation à 0.001 mm. on l'obtient entre 170° à 180° C. avec un rendement de 3.5 g. ou 12%. Calculé pour  $C_{20}H_{15}O_2N$ : N, 4.6%. Trouvé: N, 4.8%.

*4-Méthyl-4'-nitrostilbène (I, R = p-méthyl) (16)*

La réaction de Meerwein entre l'acide *p*-nitrocinnamique (0.1 mole) et le sel de diazonium provenant de la *p*-toluidine (0.1 mole) s'effectue entre 15° et 22° C. La trituration du produit de la réaction avec une petite quantité d'acide acétique glacial donne le 4-méthyl-4'-nitrostilbène qui cristallise de l'alcool éthylique en lamelles jaune pâle de point de fusion 152° à 153° C. Rendement, 3.2 g. ou 14%. Calculé pour  $C_{15}H_{13}O_2N$ : N, 5.8%. Trouvé: N, 5.8%.

*3-Nitro-4'-chlorostilbène (II, R = p-chloro)*

La solution du chlorure de *p*-chlorobenzènediazonium (0.1 mole) réagit avec une solution d'acide *m*-nitrocinnamique (0.1 mole) dans l'acétone (600 ml.) dans les conditions habituelles. Le dégagement gazeux commence vers 5° C. et persiste pendant deux heures entre 12° et 15° C. Le produit de la réaction est pulvérisé, lavé plusieurs fois à l'ammoniaque 2 N, puis à l'eau et séché. Le 3-nitro-4'-chlorostilbène cristallise par trituration à l'acide acétique. Recristallisé de l'éthanol, il apparaît sous la forme d'aiguilles jaunes de point de fusion 122° à 123° C. Le rendement du produit pur est de 3.0 g. ou 12%. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé N, 5.3%.

**3-Nitro-4'-bromostilbène (II, R = *p*-bromo)**

La réaction de Meerwein est effectuée comme dans le cas précédent à partir de la *p*-bromaniline (17.2 g., 0.1 mole) et de l'acide *m*-nitrocinnamique (0.1 mole). Le 3-nitro-4'-bromostilbène cristallise par trituration à l'acide acétique. Il est purifié par recristallisation de l'alcool éthylique avec traitement au noir animal. Il se présente sous la forme de fines aiguilles jaunes de point de fusion 118° C. Rendement, 3.0 g. ou 10%. Calculé pour  $C_{14}H_{10}O_2NBr$ : N, 4.6%. Trouvé: N, 4.7%.

**2-Chloro-3'-nitrostilbène (II, R = *o*-chloro)**

La copulation entre l'acide *m*-nitrocinnamique (0.1 mole) et le sel de diazonium dérivé de l'*o*-chloraniline (0.1 mole) s'effectue en trois heures à une température optimum de 20° C. Le résidu de la distillation à la vapeur d'eau est extrait au benzène. La solution benzénique est lavée à l'ammoniaque 2 *N*, puis à l'eau et séchée sur du sulfate de sodium anhydre. L'évaporation du solvant laisse le 2-chloro-3'-nitrostilbène brut qui se sublime à 140° à 150° C. (0.001 mm.) et cristallise de l'alcool éthylique sous forme d'aiguilles jaune pâle de point de fusion 108° C. Rendement, 4.5 g. ou 17%. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé: N, 5.4%.

Par réaction entre l'acide *o*-chlorocinnamique (0.1 mole) et le sel de diazonium dérivé de la *m*-nitraniline (0.1 mole) en trois heures entre 6° et 12° C. on obtient également le 2-chloro-3'-nitrostilbène qui est isolé de la même façon, mais avec un rendement de 6.5 g. ou 25%. Point de fusion mixte, 108° C. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé: N, 5.3%.

**3-Nitro-4'-méthoxystilbène (II, R = *p*-méthoxy)**

La solution aqueuse du chlorure de *p*-méthoxybenzènediazonium (0.1 mole) réagit avec un mélange contenant une fraction de mole égale d'acide *m*-nitrocinnamique, dans les conditions employées au cours des expériences précédentes. La réaction commence vers 5° C., mais elle est très lente à basse température. Elle se complète en trois heures à une température voisine de 25° C. obtenue en plaçant temporairement le mélange réactionnel dans un bain d'eau tiède. Le produit de la réaction est débarrassé des composants volatils par la distillation à la vapeur d'eau et extrait au benzène. La solution benzénique est lavée à l'ammoniaque 2 *N*, puis à l'eau. Après l'évaporation du solvant, le 3-nitro-4'-méthoxystilbène distille à 160° à 175° C. (0.005 mm.) sous la forme d'une huile rougeâtre qui cristallise de l'alcool en lamelles jaune pâle de point de fusion 91° C. Rendement, 3.0 g. ou 12%. Calculé pour  $C_{15}H_{13}O_3N$ : N, 5.5%. Trouvé: N, 5.5%.

**2-Méthoxy-3'-nitrostilbène (II, R = *o*-méthoxy)**

La réaction de Meerwein entre l'acide *m*-nitrocinnamique (0.1 mole) et le sel de diazonium de l'*o*-anisidine (0.1 mole) débute à 20° C. et se prolonge durant cinq heures à 30° à 35° C. Le 2-méthoxy-3'-nitrostilbène est isolé du produit de la réaction de la même façon que le 3-nitro-4'-méthoxystilbène. Il distille à 130° à 140° C. (0.005 mm.) et cristallise de l'alcool en lamelles

effeuillées jaune serin de point de fusion  $87^{\circ}$  à  $88^{\circ}$  C. Rendement, 2.0 g. ou 8%. Calculé pour  $C_{15}H_{13}O_3N$ : N, 5.5%. Trouvé: N, 5.4%.

Le même 2-méthoxy-3'-nitrostilbène s'obtient en faisant réagir l'acide *o*-méthoxycinnamique (0.1 mole) et le chlorure de *p*-nitrobenzène diazonium (0.1 mole) et en isolant le produit de la réaction de la même façon. Le rendement est de 6.0 g. ou 25%. Le point de fusion du 2-méthoxy-3'-nitrostilbène ainsi obtenu est de  $88^{\circ}$  C. Un point de fusion mixte donne le même résultat.

*3-Nitro-4'-méthylstilbène (II, R = p-méthyl)*

La copulation entre l'acide *m*-nitrocinnamique (0.1 mole) et le sel de diazonium provenant de la *p*-toluidine (0.1 mole) débute vers  $15^{\circ}$  C. et se prolonge durant deux heures entre  $20^{\circ}$  à  $25^{\circ}$  C. Le 3-nitro-4'-méthylstilbène est isolé du produit de la réaction de la même façon que le 3-nitro-4'-chlorostilbène. Il cristallise de l'alcool sous forme de longues aiguilles jaune citron de point de fusion  $99^{\circ}$  C. Rendement, 2.5 g. ou 10%. Calculé pour  $C_{15}H_{13}O_2N$ : N, 5.8%. Trouvé: N, 5.7%.

*3-Nitro-2'-méthylstilbène (II, R = o-méthyl)*

La réaction entre l'acide *m*-nitrocinnamique (0.1 mole) et le sel de diazonium dérivant de l'*o*-toluidine (0.1 mole) commence vers  $20^{\circ}$  C. et se poursuit pendant trois heures à  $25^{\circ}$  à  $28^{\circ}$  C. Le 3-nitro-2'-méthylstilbène est isolé du produit de la réaction par extraction au benzène. Il distille à  $100^{\circ}$  à  $120^{\circ}$  C. (0.005 mm.) et cristallise de l'alcool en petits prismes jaune citron de point de fusion  $86^{\circ}$  C. Rendement, 1.0 g. ou 5%. Calculé pour  $C_{15}H_{13}O_2N$ : N, 5.8%. Trouvé: N, 5.8%.

*2-Chloro-2'-nitrostilbène (III, R = o-nitro)*

Le chlorure de l'*o*-nitrobenzène diazonium (0.1 mole) réagit avec l'acide *o*-chlorocinnamique (0.1 mole) dans l'acétone (600 ml.) dans les conditions habituelles. Le dégagement gazeux se produit entre  $6^{\circ}$  et  $12^{\circ}$  C. et se termine après trois heures d'agitation mécanique. Le solide brun, obtenu en suivant la méthode d'isolation du 4-chloro-4'-nitrostilbène, cristallise de l'acide acétique après traitement au noir animal. Le 2-chloro-2'-nitrostilbène est un solide jaune serin cristallisant en fines aiguilles de point de fusion  $110^{\circ}$  à  $111^{\circ}$  C. Rendement, 2.0 g. ou 8%. Calculé pour  $C_{14}H_{10}O_2NCl$ : N, 5.4%. Trouvé: N, 5.3%.

*2,2'-Dichlorostilbène (III, R = o-chloro)*

La solution du chlorure de l'*o*-chlorobenzènediazonium (0.1 mole) réagit avec l'acide *o*-chlorocinnamique (0.1 mole) dans les conditions habituelles. La réaction débute immédiatement vers  $6^{\circ}$  C. et persiste pendant deux heures, sous une vigoureuse agitation mécanique, à  $15^{\circ}$  à  $18^{\circ}$  C. Du résidu brun gommeux isolé après la réaction le 2,2'-dichlorostilbène cristallise de l'acide acétique dilué, puis de l'alcool absolu sous la forme de fines aiguilles rose très pâle de point de fusion  $97^{\circ}$  à  $98^{\circ}$  C. Rendement, 3.0 g. ou 12%. Calculé pour  $C_{14}H_{10}OCl_2$ : Cl, 28.7%. Trouvé: Cl, 28.5%.

*2,4'-Dichlorostilbène (III, R = p-chloro)*

La réaction entre le chlorure du *p*-chlorobenzène diazonium (0.1 mole) et l'acide *o*-chlorocinnamique (0.1 mole) débute vers 6° C. et est complétée après trois heures d'agitation entre 10° et 15° C. Le 2,4'-dichlorostilbène cristallise d'abord de l'acide acétique, puis de l'alcool absolu sous la forme de fines aiguilles blanches de point de fusion 71° C. Rendement, 7.0 g. ou 28%. Calculé pour  $C_{14}H_{10}Cl_2$ : Cl, 28.7%. Trouvé: Cl, 28.6%.

*2-Chloro-4'-bromostilbène (III, R = p-bromo)*

La réaction entre l'acide *o*-chlorocinnamique (0.1 mole) et le chlorure de *p*-bromobenzène diazonium (0.1 mole) commence vers 8° C. et se complète en trois heures d'agitation à 15° à 18° C. Après la distillation à la vapeur d'eau le produit de la réaction est extrait au benzène. La solution benzénique est évaporée après lavage à l'ammoniaque 2 *N* et le 2-chloro-4'-bromostilbène est distillé à 115° à 125° C. (0.005 mm.). Cristallisé de l'alcool, il apparaît sous forme de plaques brillantes jaune très pâle de point de fusion 85° à 86° C. Rendement, 5.0 g. ou 17%. Calculé pour  $C_{14}H_{10}ClBr$ : Hal., 39.3%. Trouvé: Hal., 39.0%.

*2-Chloro-4'-phénylstilbène (III, R = p-phényl)*

La réaction de Meerwein entre le sel de diazonium obtenu du *p*-amino-diphényle (16.9 g., 0.1 mole) et l'acide *o*-chlorocinnamique (0.1 mole) opérée dans les conditions habituelles, débute vers 12° C. et est terminée après quatre heures d'agitation à 20° à 25° C. Du solide isolé du produit de la réaction par le procédé ordinaire le 2-chloro-4'-phénylstilbène se sublime vers 200° C. (0.005 mm.). Il cristallise de l'alcool sous forme de plaques jaunâtres de point de fusion 135° C. Rendement, 3.5 g. ou 12%. Calculé pour  $C_{20}H_{15}Cl$ : Cl, 12.2%. Trouvé: Cl, 12.2%.

*2-Chloro-4'-méthoxystilbène (III, R = p-méthoxy) (2)*

La copulation de type Meerwein entre le chlorure de *p*-méthoxybenzène diazonium (0.1 mole) et une fraction de mole équivalente d'acide *o*-chlorocinnamique s'effectue en trois heures entre 20° et 25° C. Les composants volatils du mélange résultant sont entraînés par une distillation à la vapeur d'eau et le résidu est extrait au benzène. La solution benzénique est lavée à l'ammoniaque 2 *N*, puis à l'eau et le solvant évaporé au bain-marie. Le 2-chloro-4'-méthoxystilbène distille à 100° à 110° C. (0.005 mm.). Recristallisé de l'alcool méthylique il apparaît sous la forme de prismes de couleur jaune pâle de point de fusion 62° C. Rendement, 3.0 g. ou 12%. Calculé pour  $C_{15}H_{13}Cl$ : Cl, 15.5%. Trouvé: Cl, 15.3%.

*2-Chloro-2'-méthoxystilbène (III, R = o-méthoxy)*

La réaction entre l'acide *o*-chlorocinnamique (0.1 mole) et le sel de diazonium dérivant de l'*o*-anisidine (0.1 mole) se passe entre 30° et 35° C. Le résidu de la distillation à la vapeur d'eau est extrait au benzène et le 2-chloro-2'-méthoxystilbène est isolé de la façon habituelle. Il distille à 85° à 90° C. (0.005 mm.) sous la forme d'une huile qu'il a été impossible de cristalliser.



*2,2'-Diméthoxystilbène (IV, R = o-méthoxy) (10)*

Le chlorure d'*o*-méthoxybenzènediazonium (0.1 mole) réagit avec l'acide *o*-méthoxycinnamique (0.1 mole) dans l'acétone (1000 ml.) selon les conditions de Meerwein. La réaction dure trois heures entre 12° et 15° C. Du résidu solide isolé du produit de la réaction le 2,2'-diméthoxystilbène se sublime entre 140° et 150° C. (0.001 mm.) et cristallise du méthanol en petites aiguilles jaune orange de point de fusion 136° C. Rendement, 1.8 g. ou 8%. Calculé pour  $C_{16}H_{16}O_2$ : C, 79.9; H, 6.7%. Trouvé: C, 79.4; H, 6.5%.

*2,4'-Diméthoxystilbène (IV, R = p-méthoxy) (20)*

Du chlorure de *p*-méthoxybenzènediazonium (0.1 mole) et de l'acide *o*-méthoxycinnamique (0.1 mole) par la réaction de Meerwein à 15° à 25° C. est obtenu en trois heures le 2,4'-diméthoxystilbène qui distille à 170° à 180° C. (0.005 mm.) (température du bain) et cristallise de l'alcool sous forme de feuillets blancs de point de fusion 94° à 95° C. Rendement, 5.0 g. ou 21%. Calculé pour  $C_{16}H_{16}O_2$ : C, 80.0; H, 6.6%. Trouvé: C, 79.5; H, 6.8%.

*2-Méthoxy-4'-chlorostilbène (IV, R = p-chloro)*

Le chlorure de *p*-chlorobenzènediazonium (0.1 mole) réagit à froid avec l'acide *o*-méthoxycinnamique (0.1 mole) et la réaction persiste pendant deux heures à 10° à 15° C. Le 2-méthoxy-4'-chlorostilbène est isolé par l'extraction au benzène. Il distille à 95° à 100° C. (0.005 mm.) et cristallise de l'alcool éthylique en aiguilles jaune pâle de point de fusion 83° à 84° C. Rendement, 2.0 g. ou 8%. Calculé pour  $C_{15}H_{13}OCl$ : Cl, 14.5%. Trouvé: Cl, 15.0%.

*2-Méthoxy-4'-phénylstilbène (IV, R = p-phényl)*

La réaction de Meerwein entre l'acide *o*-méthoxycinnamique (0.1 mole) et le sel de diazonium dérivant du *p*-aminodiphényle (0.1 mole) s'effectue en trois heures à 20° à 25° C. Du solide isolé du produit de la réaction le 2-méthoxy-4'-diphénylstilbène se sublime à 125° à 130° C. (0.001 mm.) et cristallise de l'alcool sous la forme de petits prismes blancs de point de fusion 184° à 185° C. Rendement, 10.0 g. ou 35%. Calculé pour  $C_{21}H_{18}O$ : C, 88; H, 6.3%. Trouvé: C, 87.5; H, 5.8%.

*2-Méthoxy-4'-bromostilbène (IV, R = p-bromo)*

La copulation entre l'acide *o*-méthoxycinnamique (0.1 mole) et le sel de diazonium de la *p*-bromaniline (0.1 mole) prend deux heures entre 20° et 30° C. Du solide obtenu du produit de la réaction le 2-méthoxy-4'-bromostilbène distille à 95° à 100° C. (0.005 mm.) et cristallise de l'alcool en longues aiguilles jaune pâle fondant à 88° à 89° C. Rendement, 4.0 g. ou 13%. Calculé pour  $C_{15}H_{13}OBr$ : Br, 27.7%. Trouvé: Br, 28.2%.

*2-Méthoxy-2'-nitrostilbène (IV, R = o-nitro)*

La réaction de Meerwein entre l'acide *o*-méthoxycinnamique (0.1 mole) et le sel de diazonium obtenu de l'*o*-nitraniline (0.1 mole) dure une demi-heure entre 8° et 12° C. Le mélange résultant est soumis à la distillation à la vapeur d'eau et le résidu est lavé à l'ammoniaque 2 *N*, puis extrait au benzène. L'évaporation du solvant laisse le 2-méthoxy-2'-nitrostilbène qui distille vers



90° C. (0.005 mm.) et cristallise de l'alcool sous la forme d'aiguilles jaunes de point de fusion 81° à 82° C. Rendement, 2.1 g. ou 5%. Calculé pour  $C_{15}H_{13}O_3N$ : C, 70.5; H, 5.3%. Trouvé: C, 70.2; H, 5.7%.

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## THE CATALYTIC ACTION OF ALUMINIUM SILICATES

### II. THE DEHYDRATION OF BUTANEDIOL-1,3 AND BUTANEDIOL-1,4 OVER ACTIVATED MORDEN BENTONITE<sup>1</sup>

BY A. N. BOURNS<sup>2</sup> AND R. V. V. NICHOLLS

#### Abstract

The dehydration of butanediol-1,3 over activated Morden bentonite was investigated. At 250° to 350° C., the organic liquid products consisted mainly of *n*-butyraldehyde, butene-3-ol-1, and the *n*-butyral of butanediol-1,3. Formaldehyde was dissolved in the liquid products and considerable carbon was deposited on the catalyst. The gaseous products consisted of propene and butadiene-1,3, the maximum butadiene yield being 29%. Butanediol-1,4, over the bentonite catalyst, was converted to tetrahydrofuran in almost theoretical yields at 250° to 300° C. At higher temperatures, 400° to 500° C., gaseous decomposition occurred, the main products being propene and formaldehyde. Only traces of butadiene-1,3 were formed from the dry glycol while an 8% diolefin yield resulted using water as diluent.

#### Introduction

In the first paper of this series (2), an investigation of the vapor phase dehydration over activated Morden bentonite of butanediol-2,3 and its mono-dehydration product, butanone-2, was reported. Below 350° C., high yields of butanone-2 were obtained from the glycol. At higher temperatures, 650° to 700° C., using water vapor as diluent, butadiene-1,3 was formed in 25% yield. This diene also was obtained in 45% yield by passing butanone-2 over the bentonite catalyst at 700° C. in presence of water vapor. The present paper is concerned with a study of the dehydration of the glycols, butanediol-1,3 and butanediol-1,4 over this catalyst.

Numerous patents have been issued on the production of butadiene-1,3 by the vapor phase dehydration of butanediol-1,3. Among the more effective catalysts may be mentioned the phosphate salts: primary sodium phosphate, secondary calcium phosphate, acid bismuth orthophosphate and neutral pyro- or orthophosphates of the alkaline earth metals (5). Red phosphorus deposited on pumice or mixed with primary sodium phosphate also has been reported as a superior catalyst for this reaction (6). Nagai (9) has investigated the dehydration of this glycol over alumina and various clay catalysts. Less than 50% of the gaseous products consisted of butadiene-1,3, the remainder being mono-olefins which were considered a mixture of propene and butene.

The nature of the product obtained by the vapor phase dehydration of butanediol-1,4 depends upon both the type of catalyst and the temperature of the reaction (4). Thus tetrahydrofuran has been obtained in almost

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Contribution from the Division of Organic Chemistry, Department of Chemistry, McGill University, Montreal, Que.

<sup>2</sup> Holder, at the time, of a Studentship and Fellowship under the National Research Council of Canada. Present address, McMaster University, Hamilton, Ontario.

theoretical yields at 250° to 350° C. using aluminium oxide and chromium oxide. At higher temperatures, these catalysts promoted the formation of propene and formaldehyde. Acidic catalysts such as primary sodium pyrophosphate, primary and secondary calcium phosphate, and acidic oxides of tungsten and molybdenum also have been found effective for the production of tetrahydrofuran below 350° C. At higher temperatures, however, butadiene-1,3 was formed in good yield. This diene also has been obtained by the dehydration of tetrahydrofuran over the acidic type of catalyst (11).

### Experimental

#### Materials

Butanediol-1,3 was obtained from Shawinigan Chemicals Ltd. It had been fractionated through a Stedman column in the Shawinigan Research Laboratories and was used in the present investigation without further purification. The physical constants of the glycol were: b.p. 207.5° to 208° C. (760 mm.),  $d_4^{20}$  1.002,  $n_D^{20}$  1.4404.

Butanediol-1,4 was prepared by high-pressure hydrogenation of diethyl succinate over copper-chromium oxide (1). Careful fractionation of the reaction mixture gave, in 80% yield, a product: b.p. 230° C. (760 mm.),  $d_4^{20}$  1.016,  $n_D^{20}$  1.4459.

Morden bentonite, obtained from the Pembina Mountain Clays Ltd. of Winnipeg, was activated by treatment with 20% sulphuric acid according to the method described in an earlier paper (2).

#### Apparatus

The catalysis apparatus used in the present investigation is described elsewhere (7). In brief, it consisted of a liquid feed device, an iron catalyst tube heated in a vertical electric furnace, a condenser and receiver for liquid products, and a gas meter and sampling tube for gaseous products. The upper half of the catalyst tube, serving as a vaporizer and preheater, was packed with coarse steel wool while the lower half was filled with 100 gm. (about 260 ml.) of 4 to 8 mesh activated Morden bentonite. In certain experiments, water vapor was used as a diluent, in which case the glycols were diluted with the desired amount of water and the solution passed into the vaporizer.

#### Analytical Methods

The liquid products from the dry glycol experiments (conducted in the absence of water as diluent) were saturated with sodium chloride and the upper organic layer separated, dried, and given a preliminary distillation in order to remove high boiling material and tarry residue. The distillate was carefully fractionated through an 18 in. column packed with 3/32 in. glass helices. In the butanediol-1,3 experiments, prior to the preliminary distillation, the liquid products were heated under reflux to remove the dissolved gas. This was collected in a graduated aspirator and analyzed for butadiene content. The organic liquid products obtained in the water vapor runs were

not analyzed quantitatively since their solubility in the large volume of water present made a separation difficult.

Formaldehyde was detected in the liquid products from both glycols by the resorcinol test and a derivative, methylene-di- $\beta$ -naphthol, was prepared for further identification. Quantitative determination by the hydrogen peroxide method (3) gave satisfactory results when used for the organic and aqueous layers obtained from the high temperature butanediol-1,4 runs. When applied to the products from butanediol-1,3, however, this method, as well as the iodometric and sodium cyanide procedures, failed to give consistent results, although some indication of the relative amount of formaldehyde produced in each run was obtained.

The gaseous products were analyzed in a modified Bone and Wheeler apparatus. The approximate composition of the gaseous mono-olefins was determined by formation of their dibromides followed by careful fractionation under reduced pressure. *p*-Bromotoluene (b.p. 90° C. (50 mm.)) was used as the booster. Butadiene was determined volumetrically by absorption in molten maleic anhydride.

### Results

#### Dehydration of Butanediol-1,3

Experiments showing the effect of temperature, feed rate and water dilution on the dehydration of butanediol-1,3 are given in Table I. Liquid products were analyzed in the case of the dry runs only and were found to consist mainly of *n*-butyraldehyde, butene-3-ol-1, and the cyclic acetal formed by the condensation of the glycol with *n*-butyraldehyde. This compound was identified by synthesis in the liquid phase. In addition, small amounts of high boiling material and residue were obtained. Unchanged butanediol-1,3 was recovered in Run 53 only, conducted at 250° C. The physical constants obtained for the purified liquid products were as follows:

<i>n</i> -Butyraldehyde	b.p. 72-78° C. (760 mm.)		$n_D^{20}$ 1.3894
2,4-dinitrophenylhydrazone	m.p. 122.5-123.5° C.		
Butene-3-ol-1	b.p. 113.5° C. (760 mm.)	$d_4^{20}$ 0.850	$n_D^{20}$ 1.4210
<i>n</i> -Butyral of butanediol-1,3	b.p. 161.3-161.5° C. (760 mm.)	$d_4^{20}$ 0.915	$n_D^{20}$ 1.4254

The gaseous products consisted almost entirely of unsaturated hydrocarbons. The approximate composition of the mono-olefins in volume per cent as determined by fractionation of the liquid dibromides was found to be: propene 85 to 90 and butene-2 (*cis* and *trans*) 10 to 15. Analysis for formaldehyde was not quantitative although the results obtained indicated that the larger amount was produced in the water vapor runs. During the fractionation of the liquid products, a white amorphous solid, identified as paraformaldehyde, collected on the cold finger of the column head.

Examination of Table I and Fig. 1 shows that an increase in temperature greatly increased the extent of gaseous decomposition and, at the same time,

TABLE I  
DEHYDRATION OF BUTANEDIOL-1,3 OVER ACTIVATED MORDEN BENTONITE

Run No.	Dry glycol runs							Water-glycol runs				
	53	54	57	56	58	59	55	67	62	64	66	65
Temperature, °C.	250	300	300	325	325	325	350	275	300	300	300	325
Rate of glycol feed, moles per hr. per 100 ml. of catalyst	0.25	0.10	0.25	0.25	0.50	0.76	0.25	0.12	0.25	0.25	0.25	0.25
Rate of water feed, moles per hr. per 100 ml. of catalyst	—	—	—	—	—	—	—	1.92	1.28	2.56	3.84	2.56
Water formed, moles per mole of glycol	1.01	1.60	1.56	1.67	1.53	1.30	1.75	—	—	—	—	—
Vapor products, litres (S.T.P.) per mole of glycol	6.27	12.7	11.0	12.5	10.9	7.83	14.3	11.3	10.5	12.9	14.2	15.2
Main liquid products, % of theoretical yield												
<i>n</i> -Butyraldehyde	2.2	8.3	12.8	8.9	17.1	27.5	11.3	—	—	—	—	—
Butene-3-ol-1	23.7	10.3	19.6	11.8	14.4	19.0	7.9	—	—	—	—	—
<i>n</i> -Butyral of butanediol-1,3	10.2	11.1	5.3	6.8	3.4	4.9	6.4	—	—	—	—	—
Gas analysis, vol. %												
Ethylene	0.4	0.4	0.2	0.2	0.5	1.0	0.8	0.2	0.3	0.4	0.4	0.5
Butadiene-1,3	65.9	49.8	54.3	46.6	47.1	46.3	37.0	57.7	53.6	50.0	41.5	40.8
Other unsaturated hydrocarbons	33.7	46.1	42.9	49.1	47.7	48.3	54.8	40.2	44.4	46.7	46.6	54.5
Butadiene-1,3 yield, % of theoretical	18.4	28.3	26.7	26.1	23.0	16.2	23.7	29.0	25.1	28.8	26.3	27.7

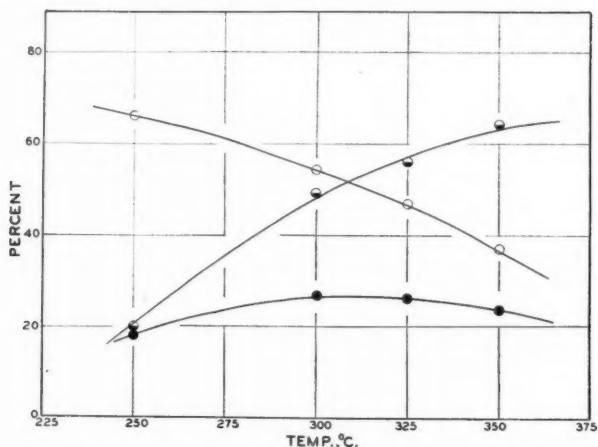


FIG. 1. The effect of temperature on the yield of butadiene-1,3 from butanediol-1,3 at a feed rate of 0.25 moles per hour per 100 ml. of catalyst (dry runs).

- Butadiene in gaseous products
- ◐ Gaseous decomposition
- Yield of butadiene

decreased the butadiene content of the gas. The over-all yield of the diene varied only slightly with temperature at any given feed rate. The results obtained using water as a diluent show that an increase in the water-to-glycol ratio increased the gaseous decomposition and decreased the butadiene content of the gas. Since considerable carbonization was observed in the dry glycol runs, the increased catalyst activity using water was probably due to removal of carbon from the surface of the catalyst by the water-gas reaction. The over-all yield was only slightly affected by dilution with water. This is in contradiction with the results of Müller-Cunradi (8), who obtained a considerable improvement in yield by the use of water.

#### Dehydration of Butanediol-1,4

Experiments showing the effect of temperature, feed rate, and water dilution on the dehydration of butanediol-1,4 are given in Table II. At 250° to 300° C., the organic product was almost pure tetrahydrofuran. Complete

TABLE II  
DEHYDRATION OF BUTANEDIOL-1,4 OVER ACTIVATED MORDEN BENTONITE

Run No.	42	43	46	41	45	47	44	48	49
Temperature, ° C.	250	250	300	300	400	450	500	500	500
Rate of glycol feed, moles per hr. per 100 ml. of catalyst	0.25	0.76	0.25	0.76	0.25	0.25	0.25	0.25	0.25
Rate of water feed, moles per hr. per 100 ml. of catalyst	—	—	—	—	—	—	—	1.28	2.56
Water formed, moles per mole of glycol	0.99	0.98	0.95	0.93	1.12	1.28	1.72	—	—
Tetrahydrofuran yield, % of theoretical	92.8	92.1	92.7	91.4	73.4	54.1	3.1	—	—
Vapor products, litres (S.T.P.) per mole of glycol	0.0	0.0	0.0	0.0	1.10	8.25	18.5	13.1	20.3
Gas analysis, vol. %									
CO <sub>2</sub>	—	—	—	—	2.9	8.1	3.6	4.1	5.2
CO	—	—	—	—	6.2	7.1	13.6	5.1	4.8
H <sub>2</sub>	—	—	—	—	5.7	12.0	6.5	6.8	9.3
Ethylene	—	—	—	—	2.3	1.6	2.7	1.0	1.0
Butadiene-1,3	—	—	—	—	7.3	8.9	2.0	13.0	15.1
Other unsaturated hydrocarbons	—	—	—	—	63.7	53.9	58.7	64.7	60.8
Saturated hydrocarbons	—	—	—	—	11.9	8.0	11.0	3.9	2.8
Butadiene-1,3 yield, % of theoretical	—	—	—	—	0.2	1.9	1.0	4.5	8.0

conversion of the glycol was obtained and no gaseous decomposition resulted. The yields of tetrahydrofuran given in this table are based on the weight of product obtained after final fractionation. Since certain losses were incurred in the purification steps, the actual yields approached theoretical. Physical constants for the purified tetrahydrofuran were: b.p. 65.6° to 65.8° C. (760 mm.),  $d_4^{20}$  0.887,  $n_D^{20}$  1.4073. At higher temperatures, 400° to 500° C., decomposition into gaseous products resulted. In addition to tetrahydrofuran, the liquid products consisted of small amounts of *n*-butyraldehyde (b.p. 74° to

76° C. (760 mm.)—2,4-dinitrophenylhydrazone, m.p. 122.5° to 123.5° C.) and considerable amounts of high boiling material. This fraction, distilling over the range 76° to 200° C., could not be separated into any single component by repeated fractionation and was thought to be a complex mixture of condensation products of formaldehyde and tetrahydrofuran. The effect of temperature on the yield of tetrahydrofuran and the extent of gaseous decomposition is shown in Fig. 2. Calculation of the latter is based on the assumption that one mole of unsaturated hydrocarbons results from the gaseous decomposition of one mole of glycol.

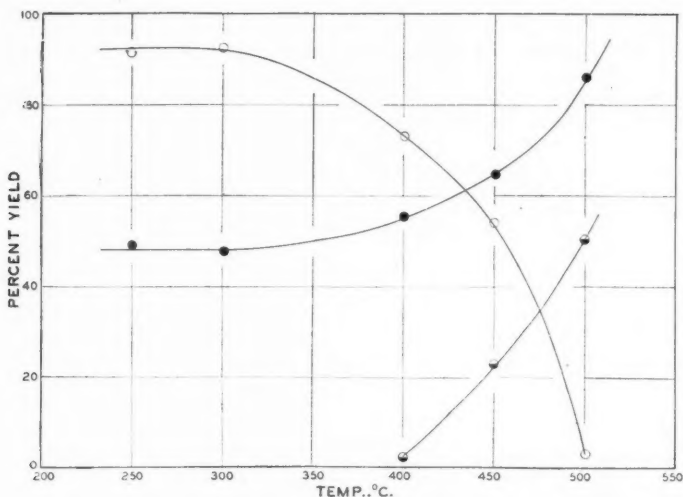


FIG. 2. Effect of temperature on the dehydration of butanediol-1,4 at a feed rate of 0.25 moles per hour per 100 ml. of catalyst (dry runs).

- Tetrahydrofuran
- Water (theoretical: 2 moles per mole of glycol)
- ◐ Gaseous decomposition

The identity of the olefinic hydrocarbons was determined by fractionation of the liquid dibromides formed from the gaseous products of Run 44. The approximate composition in volume per cent was found to be: ethene 2 to 3, propene 75 to 80, butene-2 (*cis* and *trans*) 15 to 20. Butadiene-1,3 was formed only in traces from the dry glycol, while the yield increased to 8% of the theoretical when water was used as a diluent. Formaldehyde was present in very small amounts in the liquid products from the dry glycol experiments. Using water as diluent, however, the amount of formaldehyde produced approached the theoretical calculated on the assumption that one mole of formaldehyde results for each mole of propene formed. It may be noted in this connection that considerably more high boiling material was obtained



from a dry glycol run at 500° C. than from a water-glycol run at the same temperature. This lends support to the assumption that this material resulted by condensation of formaldehyde with tetrahydrofuran.

### Discussion

#### *Butanediol-1,3*

The results obtained by the dehydration of butanediol-1,3 over activated Morden bentonite indicate that this catalyst is inferior to the acid phosphate catalysts for the production of butadiene-1,3. Two reactions compete with that leading to diene formation, one resulting in a fission of the molecule to propene and formaldehyde, the other resulting in *n*-butyraldehyde. The unsaturated alcohol, butene-3-ol-1, is probably an intermediate in the formation of both butadiene and the two fission products. Wellman (13) has found that the over-all yield of butadiene from butanediol-1,3 may be increased by recycling the liquid product, butene-3-ol-1, along with more glycol over dehydration catalysts. On the other hand, Ou Kiun-Houo (10) has reported that  $\beta$ -ethylenic alcohols of the type  $\text{RCHOHCH}_2\text{CH}=\text{CH}_2$ , when passed over alumina at 300° to 330° C., undergo fission to propene and an aldehyde. The decomposition of butene-3-ol-1 to propene and formaldehyde was cited as one example. This is consistent with Schmidt's double-bond rule, which states that a double bond between two carbon atoms strengthens the following single carbon bond and weakens the next following (12). *n*-Butyraldehyde may result by a rearrangement of butene-3-ol-1 or by a disproportionation either of this alcohol or of the original glycol.

#### *Butanediol-1,4*

The results obtained in the low temperature dehydration of butanediol-1,4 to tetrahydrofuran over activated Morden bentonite compare favorably with those previously reported using other catalysts. Furthermore, bentonite combines the features of a cheap and readily available catalyst and low temperature of dehydration. This catalyst, however, is quite ineffective for the production of butadiene-1,3 from the 1,4-glycol. The main reaction, at temperatures resulting in gas formation, are fission to propene and formaldehyde. This reaction, as in the case of butanediol-1,3, may involve butene-3-ol-1 as an intermediate. It is more likely, however, that these products result through a fission of the tetrahydrofuran ring.

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# CATALYZED NITRATION OF AMINES

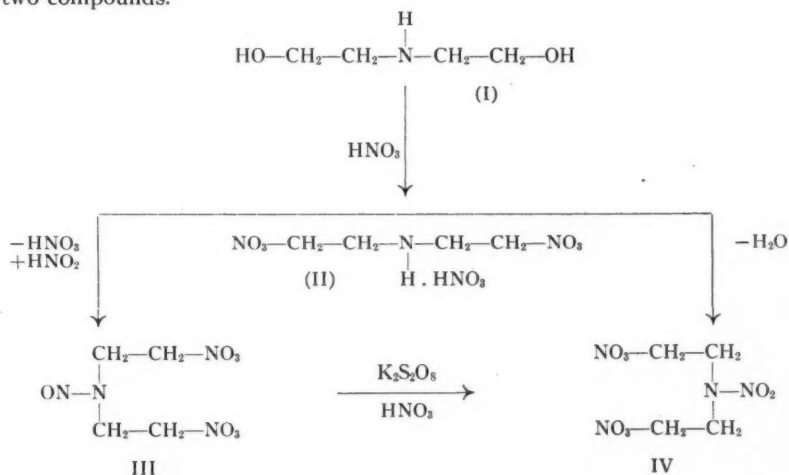
## I. DINITROXYDIETHYLNITRAMINE<sup>1</sup>

BY W. J. CHUTE,<sup>2</sup> K. G. HERRING, L. E. TOOMBS, AND GEORGE F WRIGHT

### Abstract

It has been found possible to convert diethanolamine to  $\beta,\beta$ -dinitroxydiethyl-nitramine by inclusion of hydrogen chloride or one of its salts as catalyst. The structure of this powerful explosive has been demonstrated by an alternative synthesis involving nitrosation of dinitroxydiethylammonium nitrate, followed by subsequent oxidation of dinitroxydiethylnitrosamine to the corresponding nitramine. The nitrosamine, which is unstable in boiling water, is evidently an impurity in the crude nitramine. It may be removed from the stable nitramine by blowing the suspension of molten crude product with steam. The pure explosive is a stable low-melting solid with power and detonation rate higher than those of nitroglycerin. Its insensitiveness to impact as compared with nitroglycerin recommends it as a replacement for the latter substance in explosive compositions.

Diethanolamine ought to be convertible by simple reactions into dinitroxy-diethylnitrosamine, III, or dinitroxydiethylnitramine, IV. Both of these products might be expected to be powerful explosives. Thus the latter, IV, possesses the empirical formula  $C_4H_8N_4O_8$ . This furnishes sufficient oxygen to provide complete combustion to gaseous products. Since diethanolamine is readily available it seemed worthwhile to attempt the preparation of these two compounds.



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Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont.

<sup>2</sup> Holder of a National Research Council Fellowship 1942-43.

EDITOR'S NOTE:—The subject of this paper has been released from security restrictions.

There are two steps involved in the preparation of either compound. Both require nitric acid esterification of the hydroxyl groups in diethanolamine, and this first step is not novel. Dinitroxydiethylammonium nitrate, II, has previously been reported (2) as melting at 120° C., though its preparation was not outlined in detail. We found that a better yield could be obtained by solution of diethanolamine in a large excess of absolute nitric acid than when mixed acid was used according to the patented procedure. This was largely owing to the solubility of the salt in dilute sulphuric acid. The salt was only slightly soluble in cold dilute nitric acid. When it was prepared in nitric acid alone, it was pure enough for subsequent processing. A thorough crystallization from non-aqueous solvents was required, however, if it were to be stored in the dry state necessary for its preservation. It was slightly hygroscopic and was unstable in the moist state. This nitrate salt, and also the picrate prepared for its characterization, could be detonated by impact.

A survey of the properties of this nitrate salt does not support the contention of its originators (2) that it is a useful explosive. It is, however, much more stable than its parent amine, dinitroxydiethylamine, which decomposes several hours after it is formed from the nitrate salt by treatment with aqueous alkali. The oil gradually solidifies because dinitroxydiethylammonium nitrate separates from it. This evidently involves the loss of nitric acid from dinitroxydiethylamine.

The nitrate salt, II, can be converted almost quantitatively to dinitroxydiethylnitrosamine, III, by treatment with nitrous acid. This low-melting solid is not very stable and, indeed, is destroyed completely after a few minutes in boiling water. It is 2.6 times more sensitive than TNT toward impact. It can be oxidized by ammonium persulphate in nitric acid to a low yield of another new compound, dinitroxydiethylnitramine, IV, which may be called, for convenience, by the abbreviation DINA.

By contrast to the nitrosamine, III, DINA is reasonably stable in boiling water (39% destroyed in six hours), and it may be freed from the nitrosamine after 15 min. of such treatment. DINA is comparable with cyclonite and pentaerythritol tetranitrate in power ( $1.51 \times \text{TNT}$ ) and in rate of detonation (7350 m. per sec. at density 1.47). It has a much lower melting point (52.5° C.) than either of these comparable explosives and, unlike them, is an excellent plasticizer for nitrocellulose. It is slightly less sensitive to impact than cyclonite or PETN ( $3 \times \text{TNT}$ ) and also to sympathetic detonation, but it is comparable in sensitivity toward a high-velocity rifle bullet. It cannot be ignited by burning safety fuse, and a half-inch diameter train of DINA will not burn beyond the point of ignition. Two 50-lb. boxes of DINA burn away vigorously but without detonation. It is stable at 100° C. for many hours but begins to decompose visibly at 165° C. and strongly at 180° C. DINA is decomposed rapidly by concentrated sulphuric acid at 0° C. and slowly by boiling 10% alkali. Like nitroglycerin, its induction into the human body causes violent headache, but, unlike nitroglycerin, it

is nonvolatile and hence can exert this physiological action only by absorption through the skin. No other toxic properties have been observed.

The density of DINA is 1.67 gm. per cc. at 25°C. Its heat of fusion is  $23.5 \pm 0.2$  cal. per gm. and its specific heat is  $0.38 \pm 0.02$  cal. per gm. It is non-hygroscopic. The calorific value has been determined as 1260 to 1350 cal. per gm.

The preparation of DINA via the nitrosamine was unsatisfactory owing to low yield, and a direct nitration of the amino group was sought. The direct nitration of two aliphatic amines has been reported by Bamberger and Kirpal (1), by the action of acetic anhydride on the nitrate salts of piperidine and dimethylamine, but in neither case were yields reported. Repetition of their work in our laboratory gave yields not exceeding 22 and 6% respectively for the two amines.

We were agreeably surprised, therefore, when dinitroxydiethylammonium nitrate, dried in a desiccator over calcium chloride, reacted with acetic anhydride to give a high yield of DINA. Almost as good a yield (97%) was obtained with propionic anhydride. Larger amounts of the nitrate salt, dried in an air draft, did not, however, give satisfactory yields. It was then found that the unstable nitrate salt had, in the desiccator, exchanged some of its nitric acid for hydrochloric acid from calcium chloride, and that salts of hydrochloric acid were catalysts for this nitration of aliphatic amines.

This discovery was confirmed by repetition of Bamberger and Kirpal's preparation of dimethylnitramine and nitropiperidine. When 5 mole % of zinc chloride or acetyl chloride was included, the yields were 65 and 58% respectively.\* Since Bamberger and Kirpal reported no yields, we cannot say whether they accepted low yields without comment, or whether their acetic anhydride of the year 1895 was contaminated with chloride.

Although 98% crude yields of DINA thus could be produced from the nitrate salt with acetic anhydride and zinc chloride, acetyl chloride or dinitroxydiethylammonium chloride as catalysts, the process was not ideal because of the necessity for isolation and manipulation of dinitroxydiethylammonium nitrate. We sought means of dispensing with this isolation, firstly by effecting nitramine formation in the same medium in which the nitrate salt was produced.

This medium, comprising 15 equivalents of 96% nitric acid per equivalent of diethanolamine, was treated with one equivalent of hydrogen chloride gas. The resulting orange-red solution was heated to 55°C. for 20 min. and then drowned in two liters of ice. A 47% yield of good quality DINA was obtained. The yield was lowered when less hydrogen chloride or lower temperature was used. Likewise the addition of sulphuric acid or oleum (which ought to consume the water formed by nitrate esterification) lowered the yield. It seemed impractical to add acetic anhydride because of the difficulty in

\* When this chloride-catalyzed nitration was applied to monomethylamine, an 8.5% yield of methylnitramine was obtained. The reaction with primary amines seems, however, not to be general. Only butyl acetate and butyl nitrate could be isolated by similar treatment of monobutyl amine.

recovery of acetic acid from the large nitric acid excess. The mediocre yield together with anticipation of corrosion difficulties persuaded us then to abandon this process. The method did, however, demonstrate that acetic anhydride was not necessary for aliphatic nitramine formation.

A system which maintained itself in the anhydrous state ought nevertheless to give a yield advantage. With this in mind, we tried to prepare DINA from dinitroxydiethylammonium nitrate and excess nitric acid in 95% sulphuric acid and in a solution of sulphur trioxide in acetic acid, expecting that if these were successful we could accomplish nitration by fortification of the nitrate salt solution with oleum. Although we used ample zinc chloride as a catalyst, no DINA could be isolated. This failure could not be attributed to destruction of the nitramine, since 77% of the DINA introduced into a comparable  $\text{SO}_3\text{-HNO}_3\text{-HOAc-ZnCl}_2$  system could be recovered unchanged.

We turned then to a single-stage process wherein nitric acid and diethanolamine were added proportionately to stirred acetic anhydride over a 45 min. period at 5° to 15° C. The nitric acid feed was kept slightly (2 to 4%) ahead of the other in order to insure that free amine was never present. When the nitric acid was 10% ahead of the amine, the yield was still high but the quality of product decreased. When the nitric acid feed was equivalent to, or lagged behind the other, the yield was always lowered. The catalyst, which was added at the beginning with an equivalent amount of nitric acid, was preferably a syrup prepared from 0.02 equivalent of diethanolamine and enough hydrogen chloride just to neutralize it. If this catalyst syrup were to be stored for more than two days, it was customary to only half neutralize it. Although the yield was not less when metallic chlorides or acetyl chloride was used as the catalyst, the quality of the product was inferior from the standpoint of high purity and stability required of an explosive.

While reaction temperatures as high as 30° C. can be employed, there is danger in diminution of yield owing to loss of catalyst unless the reaction vessel is sealed against dispersal of the gas phase above the reaction liquid. An increase up to 0.04 equivalent in the quantity of catalyst can be added to compensate such a loss, but larger amounts are deleterious to the quality of the product. Since such a low-quality product can finally be raised to acceptable purity by the purification method used to destroy the nitrosamine, III, it is probable that this compound, III, is the chief impurity included in the DINA by use of amounts of catalyst greater than 0.04 equivalent. Experiments wherein air was deliberately passed through the vessel during the reaction showed definitely that catalyst loss was largely (about 90%) into the gas phase. Under such circumstances it becomes advisable to maintain the lowest practical reaction temperature in a gas-tight reactor.

Since nitrosamine formation occurs concurrently with nitramine formation, a nitric acid with nitrous content between 0.08 and 0.14% should be used. The acid should also be free from chromium, nickel, and iron salts, which tend to cause an inferior product. The water content of the acid is less important since it can and should be compensated by increase in acetic anhydride.



Commercial acetic anhydride can be used in this preparation, but its acetic acid content must definitely be known in order to gauge the water absorptive power required, firstly to compensate the water in the nitric acid, and the water formed during the nitration, and secondly to stabilize the catalyst by an amount of the anhydride equivalent to the amount of hydrochloric acid used.

A good quality of diethanolamine must be used, with setting point not less than 25.5° C., and preferably as high as 27° C. Contamination with small amounts of water can be compensated by the use of more acetic anhydride than would normally be used. The presence of small amounts (1 to 3%) of monoethanolamine seems actually to be beneficial as a means of removing nitrous acid, but triethanolamine is definitely deleterious, probably because trinitroxytriethylammonium nitrate is quite unstable. An unidentified and unisolated impurity, which was encountered in one lot of commercial diethanolamine (Carbide and Carbon Chemicals, Inc.), was responsible for marked lowering in yield and quality. This impurity was found principally in the fraction boiling at 150° to 155° C. under 11 mm. pressure. The effect of any of these impurities can largely be obviated by decreasing the reaction temperature toward the lower limit of 5° C.

After addition of the reagents was completed, the mixture was then heated to 40° C. for 10 min. in order to complete the reaction. If, during this heating period, air was bubbled through the warm solution, 90 to 91% of the catalyst was removed as chlorine and nitrosyl chloride together with considerable oxides of nitrogen. While this removal of catalyst chlorine did not seem to improve the product, its removal should be desirable in order to reduce corrosion during the eventual recovery of acetic acid.

After this heating period the reaction mixture was run slowly into enough rapidly stirred and/or air blown water that the final acetic acid concentration was about 30%. If this dilution was carried out correctly in cold water, the resulting crude product was relatively easy to purify. It was filtered and washed with dilute aqueous ammonia to a pH value of 5.6 to 6.5.

The wet crude product was transferred to a steaming kettle containing water at 100° C., and steam was blown through the mixture of molten DINA and water for 15 min. When the starting materials (notably the diethanolamine) were inferior, this purification process alone was unsatisfactory, and had to be altered. The crude DINA was then suspended in 0.25% sodium carbonate instead of water and steamed for eight minutes. If the aqueous medium was not then acid (which it frequently was) enough acetic acid (about 0.3% of the total weight of aqueous phase) was introduced to remove the alkalinity. The steaming was continued for seven minutes longer. The DINA purified in this way was usually satisfactory with respect both to the Abel Heat Test and the Vacuum Stability Test (3). Treatment with alkali alone gave material which showed a good vacuum stability test but a poor Abel Test. It is of course evident that, when the steaming is carried out without addition of alkali, the purification medium will normally be acidic.



The molten DINA was then separated from the hot aqueous phase and run into sufficient acetone to effect solution. This warm solution (77° F.) in an aluminum kettle was stirred rapidly while two volumes of water at the same temperature were added as rapidly as possible together with 0.25 volume % of ammonia. The crystallization took place through slow cooling, finally to 60° F. We customarily added seed crystals during this cooling period until crystallization finally commenced. This crystallization was successful if the agitation was sufficient to prevent wall-caking and if the cooling gradient was not too high.

DINA, thus crystallized, would pack to a bulk-density of 0.8 to 0.9 with a crystal size largely between 40 and 60 mesh. A five gram sample would usually not evolve more than 4 cc. of gas in the vacuum stability apparatus (3) at 100° C. after nine hours, and the Abel Heat Test exceeded 12 min. Occasionally the product would not meet these criteria of stability until it had been ground under water or until it had been heated to its sintering point (51° C.) under vacuum. This was found to be owing to occlusion in the crystal. Such material would show proper stability after careful recrystallization or when it was wet-ground before filtration. Such wet-grinding also improved the bulk-density.

If the original ingredients were of very low quality none of these purification methods would suffice to raise the stability to an acceptable level. In this instance such material could be purified by the acetone-water crystallization after it had been maintained at 100° C. for one hour in the molten state. Although no evidence of gross decomposition was apparent during this heating period, it is undoubtedly a hazardous process which should, if possible, be avoided.

The 30% aqueous acetone recovered from the crystallization could be distilled quite safely for recovery of the solvent. The first and last fractions were slightly colored and were returned to the still. All the acetone was ammoniacal whether or not ammonia was added during the crystallization. No residual DINA separated from the residual liquor in the still. While the color in the first and last fractions could be eliminated by a prior simmering period with alkali in 6% concentration, the added trouble and expense would not seem to justify this modification.

The recovery of the acetic acid from the original reaction liquor was somewhat troublesome owing to the presence of appreciable amounts of DINA and of nitric acid. Both of these contaminants could be destroyed safely by passage of the 30% aqueous acetic acid through a stainless steel pipe heated to 193° C. under a pressure of 160 to 170 lb. per sq. in. Under these conditions, the corrosion of the stainless steel was severe and the resulting aqueous acetic acid gave strong tests for presence of iron. If, however, ethanol or butanol were added in the amount of 2% of the total volume, this corrosion was reduced until no more than a trace of iron could be detected. This finding was confirmed by corrosion tests on stainless steel samples in bomb tubes at 200° C.

The effluent aqueous acetic acid did, of course, smell strongly from the acetate esters of the alcohols which were used. Since one of the acetic esters would be used as an entrainer when the acetic acid was subsequently concentrated for reconversion to acetic anhydride, this contamination with ester would not constitute a disadvantage.

### Experimental\*

#### *Dimethylnitramine*

One mole of dimethylammonium nitrate (108 gm.) was added to 2.4 moles (230 cc.) of acetic anhydride containing 0.04 mole (5.45 gm.) of zinc chloride. After 29 hr. at 25°C., the mixture was poured into ice and water, neutralized with aqueous sodium hydroxide, and extracted with ether. The ether extract, dried with anhydrous sodium sulphate, was distilled, finally under 25 mm. at 70°C., to yield 58.6 gm. of dimethylnitramine, m.p. 57°C. This amounted to 65% of the theoretical yield. In absence of catalyst the yield was 5% of theoretical.

#### *Nitropiperidine*

Piperidine nitrate was prepared in 70% yield by neutralizing piperidine with one equivalent of 70% nitric acid at 25°C. and evaporating to dryness under 20 mm. pressure. The crude residue, 91% of theoretical, was washed with ether and then crystallized from hot absolute ethanol (4 gm. per cc.) to melt at 155° to 157°C. after ether washing and vacuum drying.

To 5 gm. (0.034 mole) of this piperidine nitrate and 0.24 gm. (0.0017 mole) of anhydrous zinc chloride was added 10 gm. (0.098 mole) of acetic anhydride. After 15 min. stirring at 25°C. to complete solution, the reaction mixture was heated to 60°C. for 30 min. with slight evolution of nitrogen oxides. The solution was then cooled and neutralized with aqueous alkali to pH 7.6. The aqueous solution was extracted 10 times with a total of 100 cc. ether. This solution, after extraction with 10% sulphuric acid (to remove piperidine), was dried with calcium chloride and evaporated to dryness. The oil was saturated with dry hydrogen chloride in order to precipitate nitrosopiperidine hydrochloride. This hydrochloride was removed by filtration and the clear oil distilled at 110° (15 mm.) as pure nitropiperidine.

This preparation was repeated in absence of the zinc chloride catalyst. A similar pair was also carried out in which the initial reaction period at 25°C. was extended over 12 hr. The yields for these experiments are tabulated below:

TABLE I  
NITRATION OF PIPERIDINE

Catalyst	% Yield after 45 min.		% Yield after 750 min.	
	Nitramine	Nitrosamine	Nitramine	Nitrosamine
ZnCl <sub>2</sub>	58	2	57	10
None	4	Trace	22	1.6

\* All melting points have been corrected against reliable standards.

*Dinitroxydiethylammonium Nitrate*

The contents of a mercury-sealed, five liter flask containing 3780 gm. (60 moles) of 99–100% nitric acid was stirred at 10° to 12° C. while 420 gm. (4.0 moles) of diethanolamine, m.p. 26.5° C., was added over a 2½ hour period. Moisture was excluded. The reaction mixture was subsequently stirred for one hour at 40° C., then poured on 6000 gm. of ice. The white crystalline precipitate was filtered immediately at the lowest possible temperature, washed with 500 cc. of ice-water, 300 cc. of ethanol, and 200 cc. of ether. The product weighed 846 gm. and melted at 118° to 119° C. after drying to constant weight in a current of air. This yield was 82% of the theoretical.

Dinitroxydiethylammonium nitrate is fairly soluble in acetone, methanol, hot solutions of ethanol, water, and nitromethane, less soluble in cold ethanol and water. It is insoluble in benzene, chloroform, ether, and petroleum ether. It shows some tendency to be hygroscopic and tends to hydrolyze when moist. Dinitroxydiethylammonium nitrate can be ignited. It burns to leave a deposit of carbon. It can be detonated by impact. Repeated crystallizations of the crude salt from methanol, ethanol, acetone, and glacial acetic acid raised the melting point to 120.5° C. Calc. for  $C_4H_{10}O_9N_4$ : C, 18.6; H, 3.91; N, 21.7%. Found: C, 18.6; H, 3.90; N, 21.7%.

*Dinitroxydiethylammonium Picrate*

This derivative was prepared from aqueous solutions of dinitroxydiethylamine nitrate and picric acid. After crystallization from water, isopropyl alcohol, and 1 : 1 toluene-ethyl acetate it melted at 136° to 137° C. Calc. for  $C_{10}H_{12}O_{13}N_6$ : C, 28.3; H, 2.85; N, 19.8%. Found: C, 28.3; H, 2.83; N, 20.1%.

*Dinitroxydiethylnitrosamine*

A solution of 17.3 gm. (0.067 mole) of dinitroxydiethylammonium nitrate in 240 cc. of water at 20° C. was stirred while 4.25 gm. (0.067 mole) of 70% nitric acid and 9.25 gm. (0.134 mole) of sodium nitrite in 20 cc. of water were added proportionately at a reaction temperature of 0° C. After 30 min. the solid product was filtered off, washed with water, and dried in vacuum to melt at 46° C. The crude yield was 14.7 gm. or 97.7% of theoretical. This material was purified by crystallization from ether-petroleum ether (b.p. 28° to 38° C.) to melt at 46° to 47° C. Calc. for  $C_4H_8N_4O_7$ : C, 21.4; H, 3.59; N, 25.0%. Found: C, 21.7; H, 3.60; N, 24.9%.

This nitrosamine was soluble in most organic solvents but was insoluble in water and petroleum ether. It gave a violet-red color by the Liebermann nitrosamine test. It was decomposed rapidly by boiling water and it slowly decomposed spontaneously at 25° C. It ignited readily and burned to leave a brown residue. Its sensitiveness to impact is 2.6 times that of TNT. Its power in the ballistic mortar is  $1.5 \times \text{TNT}$  ( $\text{RDX} = 1.61 \times \text{TNT}$ ).

*Dinitroxydiethylnitramine**A. From Dinitroxydiethylnitrosamine*

A solution of 1.0 gm. (0.0042 mole) of the nitrosamine was prepared in 10.0 gm. (0.16 mole) of 99% nitric acid at 2° to 3° C. To this solution was gradually added 2.74 gm. (0.0125 mole) of ammonium persulphate. The mixture was maintained at 0° for 15 min. after completion of addition and was then held at 25° C. for one hour. It was poured into ice to yield 0.59 gm. of material melting at 47° to 49° C. This was boiled in water for 15 min., then cooled and filtered to yield 0.35 gm. melting at 51° to 52° C. This 32% yield of the nitramine was crystallized from methanol, methanol-ether, methanol-petroleum ether (b.p. 60° to 70° C.), and acetone-water to melt at 52.5° C. after vacuum drying at 50° to 51° C. It was found that this melting point is not depressed markedly by addition of small amounts of the nitrosamine. The time-temperature cooling curve is therefore a better criterion than the melting point, and good material should show a sharp setting-point at 50.2° to 50.3° C. Calc. for  $C_4H_8N_4O_8$ : C, 20.0; H, 3.36; N, 23.3%. Found: C, 20.2; H, 3.31; N, 23.0%.

*B. From Dinitroxydiethylammonium Nitrate and Acetic Anhydride*

To a solution of 0.63 gm. (0.01 mole) of 99% nitric acid and 0.54 gm. (0.004 mole) of zinc chloride in 25.5 gm. (0.25 mole) of acetic anhydride at 25° C. was added 25.8 gm. (0.10 mole) of dinitroxydiethylammonium nitrate. The salt dissolved after the mixture was heated to 55° C. for five minutes. The solution was then poured into 60 cc. water and stirred until solidification occurred after cooling. The solid, which was filtered off and washed with water until neutral to bromocresol green, weighed 22.1 gm. (92% of theoretical) when it was dried. This crude product (melting at 49° to 51° C.) was boiled with water, after which it melted at 51° to 52° C.

The yield was slightly higher (98.3%) when a solution of 2.5 moles of 99% nitric acid in 3 moles of acetic anhydride was treated with 0.04 mole of zinc chloride and 1 mole of dinitroxydiethylammonium nitrate over a 10 min. period at 25° C. and then for 15 min. at 40° C. When propionic anhydride was used instead of acetic anhydride the yield of DINA was 97% of theoretical. Both products melted at 50° to 50.5° C. before purification.

When an attempt was made to replace the acetic anhydride with sulphuric acid or sulphur trioxide no DINA at all was obtained. In the first of these experiments 2.5 moles of 99% nitric acid, 0.06 mole of zinc chloride, and 4.24 moles of 95% sulphuric acid were used per mole of dinitroxydiethylammonium nitrate. In the second experiment, 2.5 moles of 99% nitric acid, 0.1 mole zinc chloride, 3 moles sulphur trioxide (as 35% oleum) and 4 moles of acetic acid were used per mole of dinitroxydiethylammonium nitrate. Both runs were carried out initially at 25° C. for 10 min., and then finally for 15 min. at 40° C. When DINA was used instead of the amine salt in the latter reaction mixture, 77% of it could be recovered unchanged after the same time period.

*C. From Dinitroxydiethylammonium Nitrate and Nitric plus Hydrochloric Acids*

Diethanolamine, 105 gm. (1.0 mole), was added dropwise to 954 gm. (15 moles) of 99% nitric acid while the temperature was held at 20° C. The resulting solution was cooled to 0° to 5° C. and hydrogen chloride gas was introduced until the gain in weight was 36.5 gm. (1 mole). The reaction mixture was heated at 55° C. for 20 min. and then poured on 1900 gm. of ice. The crude DINA which was filtered off weighed 100.8 gm. (42% of theoretical) and melted at 49° to 51° C. Although small yields of DINA were obtained when the hydrogen chloride was replaced by phosphorus pentachloride, phosphorus trichloride, phosgene, or chlorine, no yield at all was obtained when the hydrogen chloride was replaced by sulphuryl or thionyl chlorides.

*D. From Diethanolamine and Nitric Acid in Acetic Anhydride*

The molar ratios of diethanolamine : nitric acid : acetic anhydride : diethanolamine hydrochloride which were used are 1 : 3.2 : 3.4 : 0.05.

A 2.2 gal. stainless steel jacketed kettle fitted with thermometer and paddle stirrer (150 r.p.m.) was equipped with two graduated dropping funnels, one of which was warmed by infrared lamp radiation. The heated funnel was filled with 2 lb. of anhydrous diethanolamine and the other with nitric acid (3.96 lb. as 100% acid). Into the kettle was placed 6.88 lb. of acetic anhydride (as 100% reagent) plus 0.225 lb. extra anhydride (as 100%) for every per cent of water in the nitric acid. When the stirred anhydride was cooled as close to 40° F. as possible, 0.15 lb. of the nitric acid was added, followed by a quantity of catalyst corresponding to 0.041 lb. of diethanolamine and 0.014 lb. of hydrogen chloride. The remainder of the nitric acid and the diethanolamine were added at proportionate rates during 45 min., or to maintain the reaction temperature at 68° to 77° F. When addition was complete the temperature was increased to 104° F., maintained for 10 min., then cooled to 86° F., and run from the kettle as soon as possible. Two circumstances should be observed when this preparation is magnified to a larger scale. Firstly, the reaction at 104° F. is slightly exothermic, and the temperature in the 2 gal. kettle rose spontaneously to 113° F. unless regulated by the cooling jacket. Secondly, the DINA begins to separate when the reaction mixture is cooled to 86° F. and may cause outlet valve stoppage if flow through this valve is too long delayed.

In order consistently to avoid lumping, the kettle content should be drained into the dilution water (about 16.2 lb.) at such a rate that stirring will precipitate the crude DINA as a fine granular powder. If, therefore, dilution is to take place at a reasonable rate (30 min. per 200 gal. of liquor) the reaction liquor should be fed into a violently agitated vortex. The dilution water should be as cold as possible at the beginning since a temperature rise of about 40° to 50° F. accompanies the operation. We strongly recommend that this dilution kettle be cooled, externally if possible. These precautions seem to improve the average quality of the product, and certainly the yield of



crude DINA is about 1% higher when the dilution slurry is filtered at 40° F. rather than at 70° F.

The crude product was filtered into a canvas bag on a suction filter. It filtered with ease and was washed acid-free to bromcresol green using less than one imperial gallon of water. A final wash with dilute ammonia is beneficial. The moisture content averaged 20% and dried aliquots showed that the yield averaged 90%; m.p. 49.5° to 51.5° C. The Abel test at 100° C. averaged three minutes and the vacuum stability at 100° C. averaged 10 cc. in two hours. Milling and rewashing raised this last value to 6 cc. in eight hours, but had no effect on the Abel test.

The wet crude product was purified by adding it as rapidly as possible to 9.1 lb. of water at 212° F. The water should not be heated during this addition and is sufficient to melt all of the DINA.

If the DINA is overheated before steam is introduced, the heat test tends to be low.

Immediately after addition of the DINA, saturated steam (our pressure, 30 lb. gauge) was blown through as rapidly as possible from the extreme bottom of the kettle for 10 to 15 min. while the effluent vapor was tested for nitrous acid with starch-iodide paper. This test was usually negative after five minutes' steaming. The molten DINA was then run into 0.46 imperial gallon of acetone, and the supernatant water was run to a settling tank where, after cooling, some DINA solidified from suspension and solution.

When the diethanolamine was of poor quality, this steaming procedure yielded material which gave poor vacuum stability tests of 15 to 16 cc. of gas in eight hours at 100° C. Such substandard DINA could be improved to give vacuum stability values of 1 to 3 cc. gas in nine hours at 100° C. by using 0.26% aqueous sodium carbonate solution instead of ordinary water as the suspension medium during the steaming operation. Although the material thus purified was improved in vacuum stability, its Abel Heat Test was correspondingly lowered unless the steaming liquor was acidic at the end of the operation. This acid condition was insured by test after the first eight minutes of steaming; if it was still alkaline, acetic acid was added (maximum 13 cc.) until the water was neutral to bromcresol green.

The acetone solution of steamed DINA at 25° C. was filtered through filter-aid to remove a gummy contaminant (which tends to clog cloth filters) into a 10 gal. cylindrical aluminum kettle, 12 in. in diameter by 22 in. high, stirred by a propeller type 3 in. stirrer revolving at 1750 r.p.m. To this stirred solution was added 0.92 imperial gallon of 0.2% aqueous ammonia at 25° C. as rapidly as possible. A temperature rise of about 5° C. occurred. Rapid stirring was continued while the kettle was cooled externally with water initially at 25° C. but gradually decreasing to 15.5° C. over 20 min. while seed crystals of the monoclinic polymorph of DINA were added until crystallization was seen to occur. The purified DINA was then filtered, washed, and dried by air-draft at 40° C. to constitute a yield of 75 to 85% depending on the quality of diethanolamine used for the preparation.

*Examination of Reagents**A. Nitric Acid*

The nitric acid must have a low nitrous acid content. Since the ordinary analytical method involving oxidation with permanganate gave, in our hands, low results which made the nitric acid appear purer than actually was the case, we employed instead the method of Sutton (4, p. 306) using chloramine-T.

The nitric acid must be free from iron, chromium, or nickel salts, since these impurities markedly affect the quality of the DINA. Indeed the nitrous acid content may be critical in the preparation of DINA partly because it is presumptive for these metallic impurities. Since aluminium salts have not been found to affect the stability of DINA, the use of this metal in equipment fabrication is strongly to be recommended.

*B. Acetic anhydride*

The acetic anhydride used in this preparation gave no trouble when its acetic acid content was known. The alkaline titration was sufficiently precise for this purpose.

*C. Diethanolamine*

This is the most critical reagent used in this preparation and is the most difficult to evaluate. The setting point is, at best, an approximate criterion as is shown by the following fractionation under 11 mm. of commercial product with setting point of 25.8° C.

Fraction, %	Boiling point, °C.	Setting point, °C.
4.1	Below 142	14.7
29.5	142 - 150	27.2
57.2	150 - 153	27.3
7.4	153 - 164	26.6
1.8	Residue	24.8

The first fraction gave a strong qualitative test for monoethanolamine.

Of the two evident impurities, monoethanolamine has not proved to be deleterious except with respect to decrease in yield, especially when the reaction temperature is held closer to 15°-18° C. than 30° C. Indeed it may be beneficial in that it removes nitrous acid from the reaction medium. Triethanolamine, on the other hand, has proved to be detrimental to both yield and quality. This is understandable since its nitration product, tri-nitroxytriethylammonium nitrate is very unstable.

It is possible that a third unidentified impurity contributes to low stability. An especially unsatisfactory sample of commercial diethanolamine (setting point 24.6° C.) was distilled to remove the high boiling and low boiling fractions. The heart cut, b.p. 150° to 155° C. (11 mm.), still gave low quality DINA.



Since no satisfactory simple specification could be devised for diethanolamine, an analytical procedure involving a small scale preparation of DINA with close attention to optimum conditions was devised as the best possible test for diethanolamine quality. Since small scale crystallizations tended to be more variable than those on the large scale, the analytical sample of DINA was finely ground before the vacuum drying step which preceded the vacuum stability and Abel tests.

#### *D. Catalyst*

The catalyst was conveniently prepared by adding 1 mole of dry hydrogen chloride to 2 moles of diethanolamine in a pair of Erlenmeyer flasks connected at their bases to form a large U-shaped vessel. The rate of addition was such that the temperature did not exceed 40° C. when no external cooling was used. No solid diethanolamine hydrochloride can be isolated when hydrogen chloride is added in equimolar quantity with the diethanolamine either alone or in water, ether, or methanol solution. While the oily equimolar catalyst mixture is quite satisfactory when first prepared, it gradually precipitates a white solid, not yet identified, after several days. In order to insure a uniform catalyst mixture we therefore used the half-saturated catalyst mixture in most of our experiments.

#### *Loss and Removal of Chloride Catalyst*

There is a tendency for catalyst to be lost from the reaction mixture if an air draft prevails through the reaction flask during addition. While this is decidedly detrimental because it extends the reaction time markedly and thus permits by-product formation, it can be avoided simply by sealing the reaction vessel against any vapor loss other than that necessary because of displacement by the added reagents. The gases which are lost are chiefly nitrogen trioxide, nitrogen tetroxide, nitrosyl chloride, and chlorine.

The tendency toward such catalyst loss was utilized in the following study to remove as much of the chlorine-containing compounds as possible at the end of the reaction. The first method involved passage of air through the reaction flask and over the surface of the liquid during the simmer period at 40° C. subsequent to reaction. This air was passed through gas-washing towers containing acidified silver nitrate, so that chlorine loss could be estimated as precipitated silver chloride. This method of catalyst removal from the air space above the reaction liquor was relatively inefficient, since 300 liters of air were required per mole of diethanolamine in order to remove all but 9% of the original chlorine. The remaining 9% must be considered as fixed chlorine (possibly as acetyl chloride) since further aeration would not remove it.

The removal of catalyst was accomplished much more efficiently by bubbling the air through the reaction mixture during the simmer period at 40° C. Only three liters of air was required per mole of diethanolamine to remove all but 9% of the original chlorine. About 1% of the remainder could be removed

from the crude DINA if it was washed with 0.5% aqueous ammonia subsequent to the ordinary water-washing to pH 5.6. Under these conditions the steaming water contained only 0.01 to 0.02% of the original chlorine and none could be detected in the purified DINA.

#### *Recovery of Acetic Acid*

A 50 cc. sample of the diluted reaction liquor filtrate was heated with a stainless steel sample for one hour at 200° C. in a bomb tube. The resulting liquor was free from DINA. Distillation yielded at least 95% of the expected acetic acid, free from significant amounts of nitric, nitrous, or formic acids. The corrosion of the stainless steel was inordinately high until ethanol was added to reduce it as shown in Table II.

TABLE II  
CORROSION OF STAINLESS STEEL BY 50 CC. OF DILUTED NITRATION LIQUOR  
AT 200° C.

Addend	Rate of bite, mm. per year		
	FMB 18-8 + Ma	Staybrite 18-8	Weldanka with weld
None	10	50	15
None	6	58	15
None		53	11
1 gm. FeSO <sub>4</sub>			1.7
1 cc. ethanol		8	4
3 cc. ethanol	0.7		
10 cc. ethanol	0.3	0.4	0.2

In a larger, continuous operation the filtered dilution liquors from the DINA synthesis were mixed with 2 volume % of either ethanol or butanol and then passed through a vertical  $\frac{1}{8}$  in. I.P.S. Weldanka stainless steel pipe 26 ft. long by means of a Hills-McCanna metering pump. An air bell at the top of this pipe equalized differences in pressure. This pressure was controlled by a valve at the top of the Weldanka pipe which vented through a cooler into the receiver. The Weldanka pipe was heated throughout its vertical length by a jacket containing refluxing decalin (b.p. 193° C.).

The pressure was regulated within 5 lb. variation by manipulation of the throttling valve after the pump had been set to the correct rate of flow. The first hour's product was discarded and the next three hours of flow was considered significant. Various rates of flow were studied at pressures of 130, 160, and 170 lb. per sq. in. It was found that the four contaminants, DINA, nitric acid, nitrous acid, and formic acid were destroyed more rapidly as the pressure was raised to 170 lb. but that no further advantage was apparent up to 225 lb. Table III shows that a rate of 400 cc. per hr. through  $\frac{1}{8}$  in. pipe at 193° C. and 170 lb. per sq. in. will yield superheated aqueous acetic acid

uncontaminated with the specified four impurities. All fractions were slightly contaminated with iron, thus indicating that 2 volume % of alcohol was not quite sufficient to reduce the corrosion to an allowable limit.

TABLE III  
PURIFICATION OF DINA REACTION LIQUORS AT 193° C.

Expt. No.	Rate of pumping, cc./hr.	Pressure, lb./in. <sup>2</sup>	Test for DINA
1	100	130	None
2	200	130	None
3	300	130	Trace
4	350	130	Much
5	300	160	None
6	350	160	None
7	400	170	None
8	425	170	Trace
9	450	170	Much

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## CATALYZED NITRATION OF AMINES

II. RELATIVE BASICITIES OF SECONDARY AMINES IN ACETIC ACID<sup>1</sup>

BY G. E. DUNN, J. C. MACKENZIE, AND GEORGE F WRIGHT

## Abstract

Titration of a series of secondary amines with sulphuric or perchloric acid in acetic acid shows that those amines which do not require a chloride catalyst for their nitrations are more weakly proton-accepting than the amines which cannot be nitrated without catalyst. The weak proton-acceptance of imino-*bis*-acetonitrile which can be nitrated without catalyst is further typified by its tendency to co-ordinate with itself in 16% association in acetic acid solution. By contrast, dibutylamine, which cannot be nitrated without catalyst, is not associated in this medium.

The direct nitration of dimethylamine and piperidine was first reported by Bamberger (2) but the experimental work reported for this reaction (3) leaves some doubt whether these workers obtained adequate yields. Alternatively, their reagents might have been impure, since it has been found (4) that the nitration of dimethylamine and piperidine is catalyzed by the presence of chloride salts. Indeed adequate yields of the nitramines can be obtained from these amines only when a chloride is included in the nitration mixture.

On the other hand, a number of secondary aliphatic amines have been nitrated without catalyst. Thus imino-*bis*-acetonitrile, I, imino-*bis*-acetic acid, II, its diamide, III, and its cyclic imide, 2,6-dioxypyridazine, IV, have all been nitrated in nitric acid alone (6), and later  $\alpha,\alpha'$ -dimethyl-imino-*bis*-acetonitrile, V, was added to this list (5).

Compounds such as these five might be expected to be very weakly basic as compared with diethanolamine and, especially, with dimethylamine and piperidine. The ease with which the salts of I are hydrolyzed in water (1) confirms this expectation. The nitrations are, however, carried out in anhydrous or near-anhydrous media in which the base strengths of secondary amines are, for the most part, unknown.

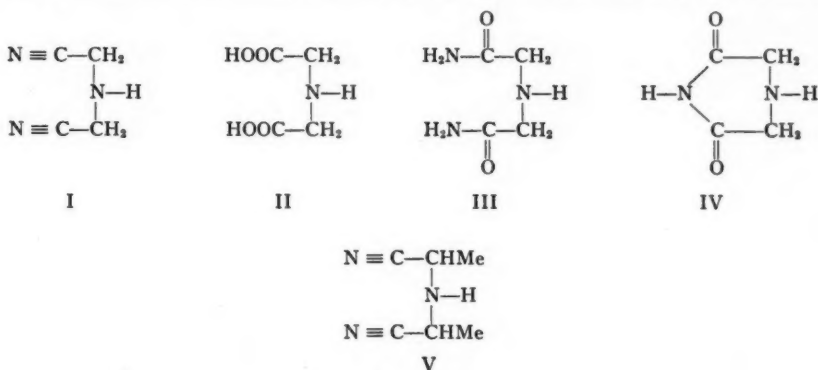
The nitrations of Franchimont and Dubsy (6) were very wasteful since they used excesses of absolute nitric acid. The acetic anhydride medium used by Bamberger (2) seemed more practical. Since this would largely be acetic acid at completion of a nitration the base strength in anhydrous acetic acid was sought as the closest possible approach to the strength of various amines in the reaction medium. The basicity in acetic anhydride could not be determined, of course, because most amines react to form acetamides.

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EDITOR'S NOTE:—The subject of this paper has been released from security restrictions.

Hall and co-workers (7, 8) have suggested a procedure for determining the proton-acquiring ability of amines in acetic acid which is based on the colorimetric method of Hammett and Deyrup (9). We have employed Hall's



colorimetric titration in a simplified form in order to determine the relative proton-acquiring ability of a series of amines which will subsequently be nitrated in an acetic acid - acetic anhydride medium.

From among the indicators used by Hall we chose *o*-nitroaniline. This indicator is largely undissociated and orange-yellow in glacial acetic acid. In sulphuric or perchloric acid of sufficient concentration to convert it to the ammonium ion it is almost colorless. If, then, an equivalent of a secondary amine is added to one equivalent of one of these acids in acetic acid containing the indicator, the ratio of undissociated (colored) indicator to total indicator will be highest when that amine of the series under test has the highest proton-acquiring ability.

Although Hall and Meyer (7) seem to have used 100% acetic acid in their studies, we found that the indicator, *o*-nitroaniline, could not entirely be decolorized by sulphuric acid in this medium. This might have been expected since the specific conductance of a 0.0388 molar solution of sulphuric acid in 100% acetic acid has been found by Kolthoff and Willman (10) to increase fourfold when 0.2% of water was added. The work of these authors thus indicates that sulphuric acid is extremely weak as a proton-donor in 100% acetic acid. In order to use *o*-nitroaniline successfully as an indicator we therefore used 99.7% acetic acid. Sulphuric acid was reasonably weak in this medium as well. Solutions equimolar with respect to the amine were therefore used in order to involve largely the first dissociable hydrogen of sulphuric acid.

Certain of the amines which we wished to test (notably the ones weakly basic in water) formed sulphates insoluble in acetic acid, and we therefore turned to perchloric acid because the salts of this acid were somewhat more soluble in acetic acid. Perchloric acid seems to be appreciably stronger than

sulphuric in this medium. The color intensity of an acetic acid solution of indicator in presence of sulphuric acid will therefore differ from the intensity of a comparable indicator solution in presence of perchloric acid. In consequence we have indicated the amine/acid titration on different graphs, Figs. 1 and 2.

We have not attempted to evaluate the extent to which the indicator associates, with acetic acid alone, as nitrophenylammonium acetate and hence

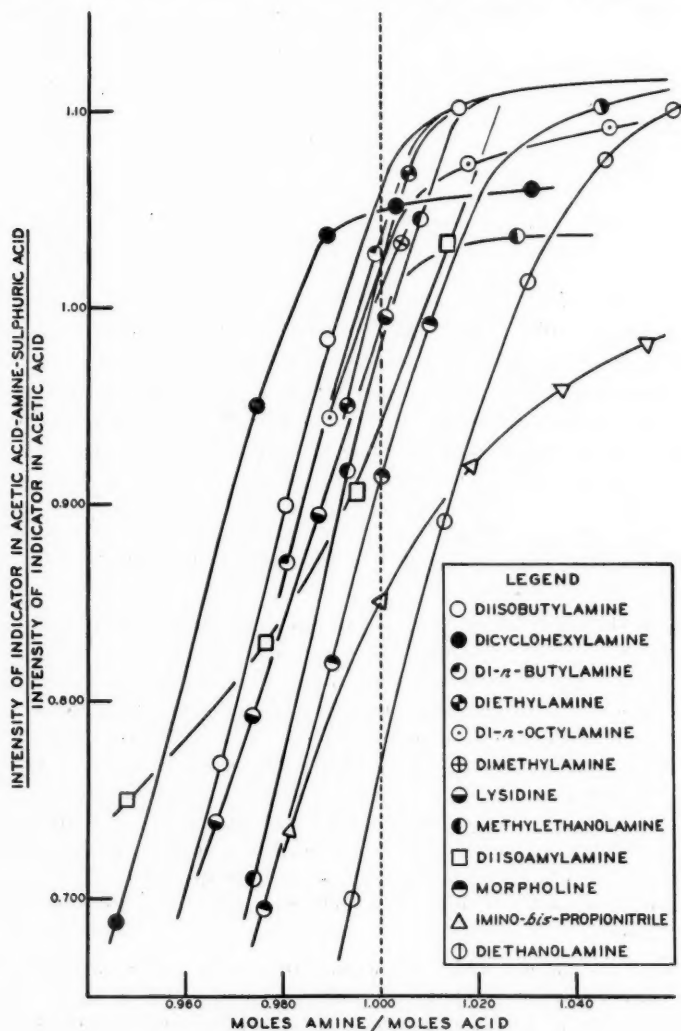


FIG. 1. Amine titration with sulphuric acid.

have expressed the titration values only as ratios of color intensity of indicator in presence of specific amounts of amine and sulphuric (or perchloric) acid versus color intensity of the same amount of indicator in acetic acid alone.

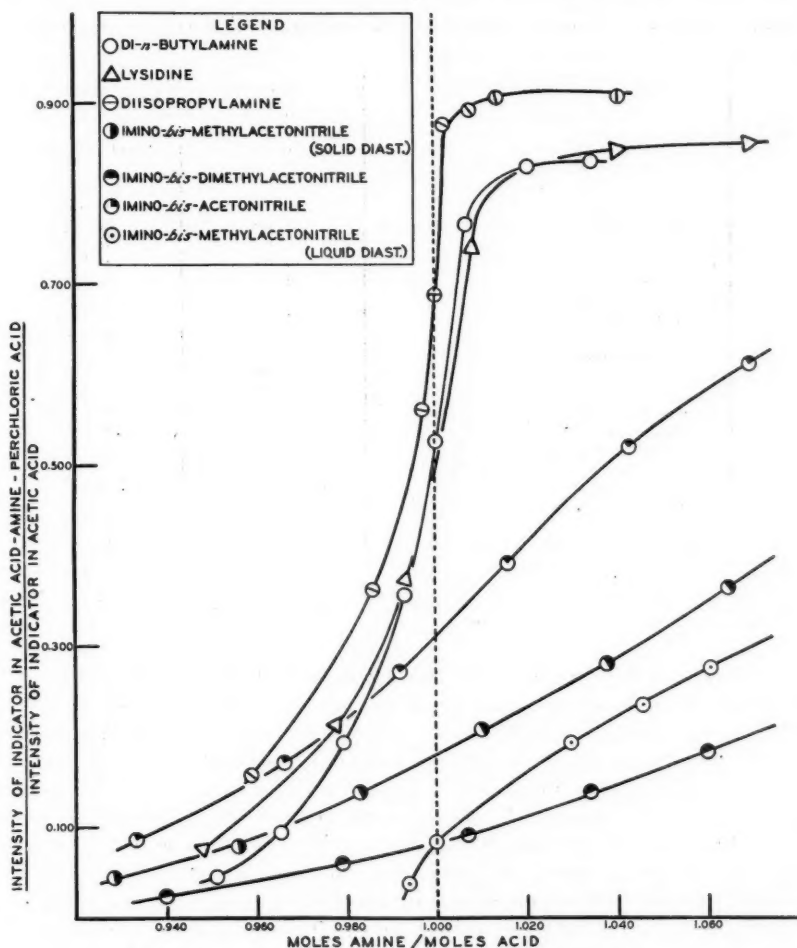


FIG. 2. Amine titration with perchloric acid.

The two series shown in Figs. 1 and 2 may be related through the values for dibutylamine and lysidine which appear in both figures. A factor of 0.506 serves to convert the indicator ratio for sulphuric acid to that of perchloric acid. Table I includes the relative values for all the amines tested with respect to both perchloric acid and sulphuric acid. Those values for amines



not titrated against perchloric acid, and which therefore represent conversion values from sulphuric titration, are indicated by the superscript c.

TABLE I  
PROTON-ATTRACTING TENDENCY WITH RESPECT TO PERCHLORIC ACID AND SULPHURIC ACID

No.	Amine	Intensity colored indicator Intensity total indicator	
		Sulphuric acid	Perchloric acid
1	Diisopropylamine		0.675 <sup>a</sup>
2	Diisobutylamine	1.06	0.536 <sup>a</sup>
3	Dicyclohexylamine	1.05	0.531 <sup>a</sup>
4	Di- <i>n</i> -butylamine	1.04	0.527
5	Diethylamine	1.02	0.516 <sup>a</sup>
6	Di- <i>n</i> -octylamine	1.02	0.516
7	Dimethylamine	1.01	0.511 <sup>a</sup>
8	Lysidine	0.99	0.500
*9	Methylethanolamine	0.98	0.495 <sup>a</sup>
10	Diisoamylamine	0.945	0.478
11	Morpholine	0.915	0.463 <sup>a</sup>
12	Imino- <i>bis</i> -propionitrile	0.85	0.430 <sup>a</sup>
13	Diethanolamine	0.77	0.389 <sup>a</sup>
14	Imino- <i>bis</i> -acetonitrile		0.310
15	Imino- <i>bis</i> -methylacetoneitrile (solid diastereomer)		0.182
16	Imino- <i>bis</i> -methylacetoneitrile (liquid diastereomer)		0.084
17	Imino- <i>bis</i> -dimethylacetoneitrile		0.0825

\* Mr. R. H. Meen of this laboratory has found that the proton-attracting tendency of piperidine is approximately that of methylethanolamine.

It will be seen from Table I that the dicyanodimethylamines (Nos. 14 to 17 incl.) are all poor proton-acceptors in acetic acid. The only questionable curve is that representing the liquid diastereomer imino-*bis*-methylacetoneitrile, V. Precipitation of perchlorate salt appeared in this instance just as the molar equivalence ratio of perchloric acid to amine was reached. In other cases, such as that of imino-*bis*-propionitrile, the perchlorate precipitated on first addition of amine so that the titration would have been completely unreliable. The sulphate salt of the amine was, however, soluble. It may thus be seen that the acids supplement one another. Actually a greater choice of acids would be desirable for future work. Thus for precise evaluation of the titration curve a weak proton-donor such as sulphuric should be used with a strong proton-acceptor such as diisopropylamine but the choice of acid must depend on the solubility of the salts in acetic acid. There are, however, limitations to the choice of titration acid in acetic acid. Thus trichloroacetic acid, strongly proton-donating in water, is much too weak in acetic acid to be of use.

Inspection of Table I shows that all those amines (Nos. 14 to 17 incl.) which will nitrate in good yield without the need for chloride catalyst (5, 6) are the

poorest proton-acceptors, while dimethylamine and piperidine (which is recovered largely after attempted nitration in absence of catalyst) occur in the order of proton-accepting ability which one might expect on the basis of the poor yields (6% and 22%) of nitro compounds which are obtained in the noncatalyzed nitration in acetic anhydride (4). There is thus some evidence to support the idea that those amines which are the poorest proton-acceptors are the most easily nitrated. Diethanolamine (Item 13, Table I) might be considered as the first of the stronger proton-acceptors in the series. Indeed this substance cannot be nitrated without catalyst (4), but it does not represent an unequivocal example. When it is introduced into nitric acid it is at once converted to dinitroxydiethylammonium nitrate. Nothing is known about the proton-accepting tendency of dinitroxydiethylamine because it is too unstable for study in the colorimetric determination. Consequently diethanolamine cannot be considered as the immediate predecessor of the nitramine which formed from it. However, the high yield of dinitroxydiethylnitramine which is produced by its nitration with a small amount of catalyst indicates that diethanolamine and dinitroxydiethylamine are intermediate between the two classes of amines which do or do not require catalyst for nitration.

A customary representation of the proton-accepting tendency of an amine is shown in the following equilibrium arrangement

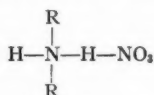


It would seem from the foregoing correlations between proton-acceptance and ease of nitration that the ammonium ion type shown at the right is not the reactive species. Indeed no reasonable concept has yet been brought forward to explain the formation of a nitrogen-nitrogen bond, either from an ammonium ion, or from the Werner co-ordination complex pictured as a hydrogen bridge.

This inadequacy is apparent in reactions other than secondary amine nitration. Thus diazotization of aromatic primary amines (11) must involve the formation of a nitrogen-nitrogen bond from a salt of the amine. It may be significant that the electron-attracting phenyl nucleus, which weakens the proton-accepting tendency of nitrogen when it replaces hydrogen in ammonia, is the typical tertiary substituent which permits the nitrogen-nitrogen bond formation found in a diazonium salt. Analogously, when the phenyl group replaces hydrogen in methylamine the resulting weaker base, methylaniline, will undergo the nitrogen-nitrogen bond formation found in nitramine formation without the necessity for a catalyst such as a chloride salt. It resembles, in this respect, the weakly proton-accepting amines of the imino-*bis*-acetonitrile type.

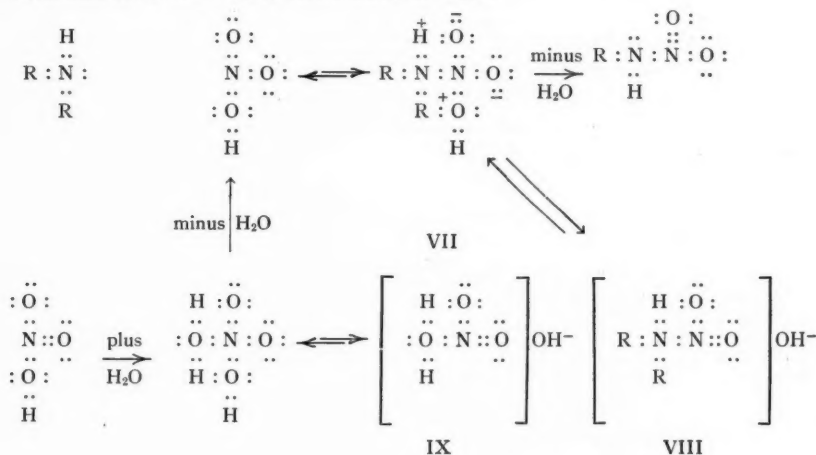
Inspection of the equilibrium outlined above does, of course, suggest that the nitration of weak bases might also proceed via the free secondary amine. There does, however, seem to be a certain necessity for salt formation as an adjunct to nitration. Thus the very weak base diphenylamine will not form a nitramine either with or without a catalyst. This may be accentuated by

nuclear nitration, which actually makes the imino group acidic in nitrated diphenylamine. Likewise diacetamides which will not form salts cannot be nitrated. A typical case is that of 2,6-dioxypyridazine, IV, wherein the dialkylamino group can be nitrated while the diacylamino group remains unchanged. On the other hand alkylacetamides, which are known to be weakly salt-forming, will nitrate with ease and without the chloride catalyst.



VI

We are prompted by these speculations to reserve the structure VI for those strongly proton-accepting secondary amines which will only nitrate well when a catalyst is used. An alternative structure for the weakly proton-accepting amines (which require no catalyst for nitration) is shown as VII, and is depicted with a nitrogen-nitrogen bond which is essentially covalent. The dipoles in such a molecule will therefore be represented as between nitrogen-oxygen and hydrogen-oxygen. Its formation is represented as owing to the strong electron-acquiring tendency of nitric acid. Its conversion to nitramine involves a *trans* elimination of water.



If one wishes to consider VII in an ionic form such as VIII, then it may be considered as the dialkylammonio derivative of the nitracidium ion shown at IX.

It will be favorable to the formation of a covalent nitrogen-nitrogen link in structure VII if the hydrogen marked (+) will be co-ordinatively linked to an oxygen marked (-), probably intermolecularly. The extent to which this dipole is real will depend on the proton-sharing tendency of the secondary

amine itself. An amine which possesses such proton-sharing proclivity ought to associate with itself in absence of a strong electron acceptor such as nitric acid.

A further contrast between the easily nitrated amines and those resistant to nitration was therefore explored by molecular weight determinations on *bis*-iminoacetonitrile, I, which will nitrate without catalyst, and dibutylamine which cannot be nitrated in the absence of chloride. The isopiestic method of Barger (as modified by Rast) showed that dibutylamine was entirely non-associated in absolute acetic acid, while the weakly basic I was 16% associated in this same medium.

If the explanation for easy nitrations which involves structure VII is valid, then it follows that a chloride catalyst must act by decreasing the proton-acquiring propensity of some secondary amines. This will be discussed in a forthcoming publication.

### Experimental

#### *Basicity Determination*

##### *A. Perchloric Acid in Acetic Acid*

A 68.6% aqueous perchloric acid solution (Smith Chemicals, 58.97 gm.) was added slowly to 105 ml. of acetic anhydride (distilled from chromic anhydride) cooled and maintained at 10° to 15° C. This solution was then adjusted with perchloric acid and acetic anhydride until no temperature change occurred on addition of either of these reagents. This slightly yellow solution was then diluted to 1100 ml. with acetic acid. This solution was standardized against crystallized potassium acetate in acetic acid using Tropaeolin 00 in acetic acid as the indicator. The molarity was thus determined as 0.3680. To 800 ml. of this perchloric acid was added 0.0950 gm. of *o*-nitroaniline (m.p. 73.0° C. corr.) to make a solution 0.0008596 molar with respect to this indicator.

##### *B. Sulphuric Acid in Acetic Acid*

A 0.3701 molar solution of 100% sulphuric acid (m.p. 10.5° C.) in 98.7% acetic acid was prepared by weighing 35 gm. of the sulphuric acid into a volumetric flask and subsequently diluting with acetic acid to 1 litre. This solution was then standardized against potassium acetate and hence with respect to the perchloric acid. Now the appropriate amount of *o*-nitroaniline (0.1187 gm. per litre of sulphuric - acetic acid) was added to give a solution 0.3701 molar with respect to sulphuric acid and 0.0008596 molar with respect to the indicator.

##### *C. Amines*

The amines were purified by crystallization and distillation procedures to remove water, ammonia, primary and tertiary amines.

##### *D. Titration*

A Klett-Summerson photoelectric colorimeter was employed and equipped with a violet filter. Since variation of 5° to 10° C. did not alter the readings

with *o*-nitroaniline-acetic acid solutions by more than 0.2%, a close temperature control was not maintained. The instrument was calibrated by readings taken on successive dilutions of a solution of *o*-nitroaniline in acetic acid, initially 0.001005 molar. This calibration should have evaluated the amount of the indicator in the colored (undissociated form) against the galvanometer reading. A typical calibration, shown in Fig. 3, indicated that the deviation from linearity expected according to Beer's law was not great. The correction for change in volume during titration (40 to about 60 ml.) was expected not to be greatly in error, and all observed values were therefore corrected to a reference volume of 60 ml.

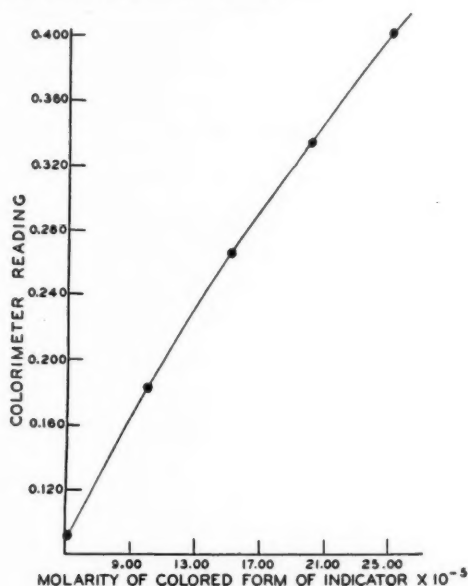


FIG. 3.

Into the cell of the colorimeter was placed 10 ml. of the acid indicator solution and then enough of a solution of amine (about 0.1 molar) in acetic acid to bring the ratio, mole amine/mole acid, to about 0.9. Successive increments of amine solution were then added until the above ratio reached 1 : 1. These amine/acid ratios were plotted against the ratio of each observed intensity to the intensity of the same amount of indicator in acetic acid alone. The data are recorded in Figs. 1 and 2. This method of titration was used in the present work in order to economize on amine, but it is recommended in consideration of greater accuracy, that dependence on extrapolation from intensity at about 40 cc. to that at 60 cc. volume be avoided by making up each separate acid/amine solution to 60 cc. volume.

*Molecular Weight Determination of Dibutylamine and Imino-bis-acetonitrile*

Dibutylamine was purified by slow fractional distillation at atmospheric pressure. After an initial fraction was discarded, the distillate, b.p. 158° to 158.5° C., was found to melt sharply at -60° to -59° C. The molecular weight of this material was determined by the Barger-Rast isopiestic method in absolute acetic acid ( $1.5 \times 10^{-3}$  % water by titration with Karl Fischer reagent). The limiting values indicate a molecular weight between 128.8 and 124.5 or between 0.3% and 3.5% dissociated.

By contrast the molecular weight of imino-bis-acetonitrile was found in acetic acid between the limits of 142-143. This represents an association, in absolute acetic acid, of 16%.

**Acknowledgment**

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## CATALYZED NITRATION OF AMINES

III. THE EASE OF NITRATION AMONG ALIPHATIC SECONDARY AMINES<sup>1</sup>

By W. J. CHUTE,<sup>2</sup> G. E. DUNN, J. C. MACKENZIE, G. S. MYERS,<sup>3</sup>  
G. N. R. SMART,<sup>4</sup> J. W. SUGGITT, AND GEORGE F WRIGHT

## Abstract

A series of secondary amines, the proton-attracting ability of which had previously been determined, have been converted to their nitramines with nitric acid and acetic anhydride. The gradation in ease of nitration has been found to vary inversely with the proton-attracting ability of the amine. Nitration becomes so difficult at an amine strength corresponding to that of diethanolamine that nitric acid and acetic anhydride alone are ineffective; a chloride catalyst must be used. The amount of this catalyst must be increased as the proton-attracting ability of the amine becomes greater until a full equivalent is required for adequate yield from the strongest amine in the series, diisopropylamine. As the nitration in the series becomes more difficult, side reactions become apparent such as nitrosation, acetylation, and fission of the secondary amine to primary amine and aldehyde. The extent of nitrosation is dependent on the concentration of catalyst, although nitrosation is not catalyzed by presence of chloride. This implies that hydrogen chloride generates nitrous acid in the reaction mixture. Acetylation is independent of presence or concentration of catalyst, but it does not occur during the formation of dicyclohexylnitramine or diisopropylnitramine. This is thought to be owing to steric hindrance from the secondary alkyl groups in these amines. Since nitracidium perchlorate has been found to be ineffective as a catalyst for this nitration, it is doubtful that nitryl chloride is the active form of the catalyst except in so far as it exists in the form of chlorine nitrite. Evidence has accumulated to show that electropositive chlorine is the effective catalyst, and that it is formed by a modification of the aqua regia reaction.

It has been found (4) that nitration of secondary amines is a general reaction if a chloride catalyst is used with those amines which resist nitration with nitric acid in anhydrous media. It was further noted (7) that the more resistant amines were stronger proton-acceptors in acetic acid than those of the imino-*bis*-acetonitrile or imino-*bis*-acetic acid type. The latter are converted easily to nitramines with nitric acid alone. While it has been shown (4) that the presence of acetic anhydride is not essential for the nitration of any secondary amine, the yield is usually higher when the anhydride is included, and sometimes it is very low without this reagent. Such a medium would become acetic acid during the nitration, so we felt justified in using this acid as a solvent in comparison of the proton-accepting tendencies of the several amines. In order to correlate these tendencies with the ease of nitration of secondary amines in general it became necessary to standardize reaction conditions. Consequently we have revised the earlier procedures (5, 11) for

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Contribution from the Chemical Laboratory, University of Toronto.

<sup>2</sup> National Research Council Fellow, 1942-43.

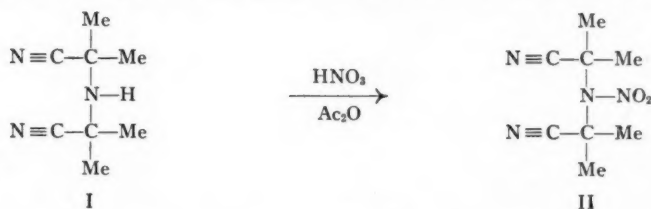
<sup>3</sup> National Research Council Fellow, 1944-45.

<sup>4</sup> Post-Doctoral Research Fellow, National Research Council.

EDITOR'S NOTE:—The subject of this paper has been released from security restrictions.

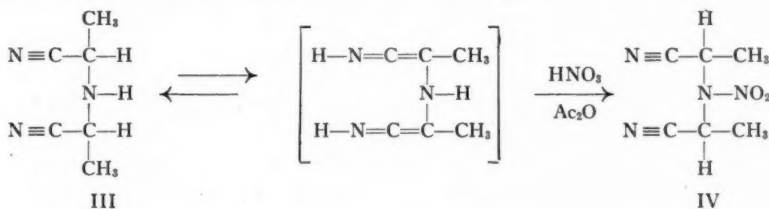


nitration of the imino-*bis*-acetonitrile type to include acetic anhydride. We have also extended this list of easily nitrated amines by nitration of imino-*bis*-dimethylacetonitrile, I, (6, 22), to give the nitramine, II. The yield of nitrimino-*bis*-acetonitrile and also the dimethyl and tetramethyl (I) analogues were all over 90% when the nitration was carried out with nitric acid and



acetic anhydride. These yields might have been expected if proton-attracting ability is inversely related to ease of nitration, since these three amines are the least basic in acetic acid of the series recently reported (7). Furthermore many of the other amines in this series have now been nitrated, as will be described in the present paper, and none of these reactions proceed satisfactorily without addition of chloride catalyst. There would thus seem to be a sudden change in behavior when the proton-accepting ability of the amine exceeds that of imino-*bis*-acetonitrile.

One might suspect that this was owing to some functional effect of the cyano group other than its influence on proton-acceptance, but two observations tend to discount this possibility. Thus one might suggest that the  $\alpha$ -cyano group permitted ephemeral rearrangement to create a vinylamine which would then conform to the aromatic type which nitrates so easily. However, if one considers imino-*bis*-methylacetonitrile, III, in this sense, he will note that this would involve racemization at the asymmetric centers.



If this isomerization occurred as a prerequisite to nitration, then the same diastereomeric mixture of nitramines should result regardless of the specific diastereomer of III which was nitrated. One of the diastereomers of III can be obtained pure, and the other almost pure. Each of these diastereomers gave its characteristic nitramine, IV, in 90% yield when it was nitrated in acetic anhydride without catalyst. Evidently no racemization and hence no isomerization took place. This result could have been predicted from the easy

nitration of imino-*bis*-dimethylacetoneitrile, I. In this case, where hydrogen is not attached to the carbon atom adjacent to the imino group, no such isomerization can occur.

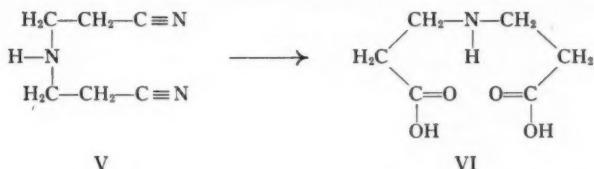
Further evidence that the cyano group was not directly responsible for the ease of nitration was furnished through imino-*bis*- $\beta$ -propionitrile. This isomer of III, with the cyano group on the carbon atom  $\beta$ , rather than  $\alpha$ , to the imino nitrogen was only slightly more proton-attracting than imino-*bis*-acetoneitrile, but it would not form  $\beta,\beta$ -dicyanodiethylnitramine unless a chloride is present in the nitric acid - acetic anhydride mixture. Inclusion of a catalytic amount of the hydrochloride salt of dicyanodiethylamine, on the other hand, enabled the formation of a 90% yield of the nitramine. The preparation does demonstrate that the cyano group is ineffective for inducing nitration unless it is attached to the carbon atom  $\alpha$  to the imino group.

This  $\beta,\beta$ -dicyanodiethylnitramine was notable because of its extremely low volatility. It resembled in this respect the  $\beta,\beta'$ -dinitroxy analogue (DINA) and this property is evidently characteristic of the beta substituent. Both of the parent amines are also relatively nonvolatile. In the case of dicyanodiethylamine the boiling point was so high that decomposition tended to occur unless fairly small amounts were distilled rapidly. Fortunately it was found that the crude undistilled amine was sufficiently pure that it could be converted into the amine salt in good yield. The salt was used in the nitration to give the pure nitramine. We were unable to obtain the nitramine in pure enough form to meet the exacting requirements of explosive technology when the amine had partially decomposed during distillation, because of a persistent impurity that was not eliminated during the nitration. This impurity was not identified. It is not  $\beta,\beta'$ -dicyanodiethylnitrosamine which melts slightly lower ( $48^\circ$  to  $48.5^\circ$  C.) than the nitramine. This nitrosamine could not be detected, even in the crude nitramine.

We were unable to determine the proton-accepting power of imino-*bis*-propionic acid (17, 18) because we were unable satisfactorily to purify the product obtained by hydrolysis of  $\beta,\beta$ -dicyanodiethylamine, V. Our product undoubtedly was contaminated with  $\beta$ -alanine or imino-*bis*-propionamide. We did determine, however, that nitration would not proceed without chloride catalyst. On the other hand, inclusion of this catalyst effected a conversion of the nitrate salt in acetic anhydride to a yield of nitramine which must have been good in view of the impurity of the initial amine. Since that amine, like  $\beta,\beta'$ -dicyanodiethylamine, V, cannot be nitrated without a catalyst it would seem that a zwitterion structure such as VI cannot contribute to ease of nitration.

Morpholine, like dicyanodiethylamine, V, would not nitrate up to  $40^\circ$  C. with acetic anhydride and nitric acid without chloride catalyst, but when 2 mole % of zinc chloride was included, the yield was over 90% of theoretical. In this instance the nitrate salt rather than the free amine was utilized, but for a different reason than that involved in the preparation of the dicyanodiethylnitramine. The nitrate salt of morpholine was used because the free amine

ignited when added to nitric acid and acetic anhydride. Even when the morpholine was diluted with acetic acid there was still evidence of decomposition. This extreme instance of amine destruction during nitration prompts



the observation that, in general, all yields of nitramines are higher when the nitrate salt is used instead of the free amine and nitric acid. However, in many cases, the difference in yield is scarcely noticeable.

An extreme instance of the difference in behavior between nitrate salt and free amine was observed in the case of diethylamine, a more strongly proton-accepting amine than morpholine. When the nitrate salt was treated at 55° C. with acetic anhydride and zinc chloride, a 60% yield of diethylnitramine was obtained, together with an 8% yield of diethylacetamide. On the other hand when diethylamine and nitric acid were added proportionately to acetic anhydride at 15° C. and the reaction was subsequently heated to 40° C. no diethylnitramine was obtained, but instead, a 34% yield of diethylacetamide. The difference in this case does not involve destruction of the amine but rather a competitive reaction between nitration and acetylation of the free amine. Prior formation of the nitrate salt seems to minimize the acetylation.

Di-*n*-butylamine is slightly more strongly proton-attracting than diethylamine, and so it too does not form a nitramine in absence of chloride catalyst. In presence of this catalyst not only the nitramine but also dibutylacetamide and dibutylnitrosamine are formed. The acetamide (23) and nitrosamine (20) have been reported previously, although neither was adequately characterized. The nitramine was unknown, so we prepared it by the method of Van Erp (26). This reaction between the potassium salt of *n*-butylnitramine and *n*-butyl iodide produces two compounds, of which the higher boiling and more stable was assumed to be the nitramine; its properties were identical with those of the compound obtained by nitration of dibutylamine, except that the product from direct nitration always was contaminated with an impurity containing chlorine. This impurity, the prevalence of which depended on the initial catalyst concentration, could be destroyed if the nitramine was boiled with 70% nitric acid.

An accurate method for separation of the three main products of the nitration reaction was devised for study of this amine. After unchanged amine was removed by washing the ether solution of the crude mixture with 2% hydrochloric acid, the dibutylacetamide could be removed because it was soluble in 12% hydrochloric acid. After evaporation of the solvent ether, the residual oil could then be freed from dibutylnitrosamine because of the

solubility of this nitrosamine in concentrated hydrochloric acid. The acetamide and nitrosamine could thus be recovered almost quantitatively. An alternative method for separating the nitramine involved the destruction of the nitrosamine with cuprous chloride (19). This method of Jones and Kenner evaluates the quantity of nitrosamine by titration of the amine formed from its decomposition. This entire separation method made it possible consistently to account for 95 to 100% of the amine used in the reaction.

The ease with which these separations could be accomplished prompted us to use this amine as a tool for evaluation of optimum conditions in the catalyzed nitration. The results of this evaluation are outlined in Table I, which describes experiments wherein amine (free or as hydrochloride salt) was added proportionately with nitric acid into stirred acetic anhydride which might or might not be diluted with acetic acid. The catalyst notation "HCl" always refers to the amine hydrochloride, which was included with the anhydride if it was in catalytic quantity, or was added proportionately if it was in stoichiometric quantity. In addition to the estimation of fate of the amine during nitration, the residual nitric acid was evaluated by strong-acid titration.

TABLE I  
NITRATION OF ONE MOLE DIBUTYLAMINE

Expt. No.	Reaction		HNO <sub>3</sub> moles	Ac <sub>2</sub> O moles	HOAc moles	Catalyst		Mole % recovery					
	Time, hr.	Temp., °C.				Type	Mole	Amine	Acet- amide	Nitros- amine	Nitra- mine	HNO <sub>3</sub>	
1	26	20	2.1	1.5	0	HCl	0.08	58	6	22	7	—	
2	24	20	1.1	1.2	0	HCl	0.08	35	13	13	23	—	
3	24	20	1.1	1.2	10	HCl	0.10	4	9	24	60	26	
4	2	20	1.1	1.2	10	HCl	0.10	43	9	23	20	77	
5	3	20	1.1	1.2	10	HCl	0.10	60	6	16	14	55	
6	24	20	1.1	1.2	10	HCl	0.10	16	3	21	54	39	
7	2	30	1.1	1.2	10	HCl	0.10	41	2	22	29	59	
8	24	30	1.1	1.2	10	HCl	0.10	11	2	23	60	21	
9	72	30	1.1	1.2	10	HCl	0.10	—	—	—	—	21	
10	26	20	4.0	16	0	HCl	0.30	0	10	42	39	—	
11	24	20	1.1	5	0	HCl NH <sub>4</sub> NO <sub>3</sub>	0.10 0.10	1.5	11	48	39	—	
12	24	20	2.2	1.2	10	HCl	0.10	30	9	12	39	—	
13	3	20	1.1	1.2	10	Cl <sub>2</sub>	1.0	36	3	19	41	77	
14	24	20	1.1	1.2	10	Cl <sub>2</sub>	1.0	7	3	21	66	38	
15	2	20	1.1	1.2	10	H <sub>2</sub> O <sub>2</sub>	0.2	74	9	6	0	—	
16	84	20	1.1	1.2	10	H <sub>2</sub> O <sub>2</sub>	0.2	61	10	22	0	—	
17	2	20	1.1	1.2	10	H <sub>2</sub> O <sub>2</sub> HCl	0.2 0.1	59	4	16	21	—	
18	24	20	1.1	1.2	10	H <sub>2</sub> O <sub>2</sub> HCl	0.2 0.1	42	4	17	32	—	
19	24	0	2.1	2.2	0	HCl	1.0	30	5	24	27	—	
20	24	20	2.1	2.2	0	HCl	1.0	5	6	17	65	—	
21	22	20	1.2	2.2*	0	HCl	0.1	11	5*	41	38	—	

\* The butyric rather than the acetic radical is involved here.

It might at first be inferred from Expts. 1 and 2 that a significant excess of nitric acid over amine tends to depress the yield of nitramine and increase the yield of nitrosamine, but the nitramine yield in this event depends also on the amount of catalyst used. Thus Expt. 1, when compared with Expt. 10, shows that the excess of catalyst will alleviate the harmful effect of excess nitric acid, although the yield of nitrosamine likewise increases. The formation of nitrosamine must necessarily involve presence of nitrous acid or a nitrite (no other source of nitrosamine is known; thus tetranitromethane is actually a nitrite ester) and we sought to decrease the nitrous acid content by decreasing the nitric acid and including ammonium nitrate (Expt. 11). Although this does not affect the nitramine yield it raises slightly rather than lowers significantly the nitrosamine yield. On the other hand, when we allow the nitric acid excess to remain high, but decrease the acetic anhydride and attenuate it with acetic acid (Expt. 12) the yield of nitrosamine is decreased markedly with respect to the nitramine yield. This latter yield is actually the same in Expts. 11 and 12. It would seem therefore that high acetic anhydride concentration and content favor high nitrosamine yield more than does an excess of nitric acid.

The attenuating effect of diluent acetic acid has generally a profound effect on the nitration. Thus Expts. 2 and 3 differ principally only in a large dilution with acetic acid in the latter. The effect of this dilution, which nearly trebles the nitramine yield while it doubles the nitrosamine yield, was observed sufficiently often that such dilution finally became standard procedure.

There is abundant evidence to show that the formation of nitramine is a relatively slow reaction (compare Expts. 3 and 4) while nitrosamine formation is much more rapid. This is seen again by comparison of Expts. 4 and 7, where reaction temperature was varied. The nitration is, however, effectively finished in less than 24 hr., since the yields of nitramine and nitrosamine are essentially the same in Expts. 3 and 8. Expts. 5 and 6 likewise illustrate the differences in rate and serve, as well, to show what reproducibility one can expect in these experiments.

An answer as to the origin of the nitrosamine may be gained from Expts. 15 to 18. Hydrogen peroxide is certainly not a nitration catalyst, and it may even retard catalyzed nitration as indicated in Expts. 17 and 18. In these experiments the nitrosamine yield was approximately a mean between the usual extremes of Expts. 12 to 24. In Expts. 15 and 16 the chloride catalyst was excluded, but not the hydrogen peroxide. As might be expected, no nitramine was formed. The nitrosamine yield was, however, also low at the end of two hours, although it gradually increased to approach the 24% level at the end of 24 hr. This must mean that, although the nitrosation is not chloride-catalyzed, the chloride catalyst must react to furnish nitrous acid at the beginning of the nitration. No other source seems to explain the high nitrosamine yield in the two hour Expt. 4 as contrasted to Expt. 15. In a longer reaction such as Expt. 16, the nitrous acid may be furnished from another source, possibly by the slow decomposition of nitric acid in acetic anhydride.

There is some evidence to indicate that the true catalyst is not stable, but suffers decomposition during the reaction. This is apparent throughout the series in Table I, if one considers the amounts of unchanged amine and nitric acid remaining at the end of reactions wherein modest yields of nitramine are obtained. The instability of the catalyst is further exemplified by Expts. 19 and 20, where full molar equivalents of dibutylamine hydrochloride were used instead of the free amine. It is evident by comparison of these two experiments that the temperature coefficient of the catalyzed reaction is such that an attempt to preserve the catalyst by lowering the reaction temperature is futile since the nitration rate is decreased inordinately. Expt. 20 must be compared with Expt. 2, since diluent acetic acid is used in neither. The nitramine yield in Expt. 20 is nearly three times as great as that in Expt. 2. It is, indeed, the highest in the series except for those recorded in Expts. 13 and 14, wherein full equivalents of chlorine were added during the two-hour addition periods.

The potency of chlorine as a catalyst suggests that electropositive chlorine might indeed be the real accelerator in the hydrogen chloride-catalyzed nitration. Its formation *in situ* could be considered as owing to oxidation of the hydrogen chloride by nitric acid. The vagaries of the aqua regia reaction would thus explain the destruction of catalytic amounts of chloride catalyst, and would as well explain the formation of nitrous acid (and hence nitrosamine) from the catalyst. Evidence for these ideas may be cited from iodometric titrations of aliquots from Expt. 20, which showed a positive chlorine titration increasing to 0.06 mole % after addition was  $\frac{1}{2}$  complete and thereafter decreasing slowly to 0.03 mole % at the end of addition. The nitrous acid in the analytical aliquot had, of course, been destroyed by sulphamic acid prior to titration.

While no great regularity seems to prevail with respect to the yields of dibutylacetamide, they tend to depend jointly on the initial quantity of the acetic anhydride and on its concentration. The formation of the acetamide is not catalyzed by chloride, and one may expect that, when the catalyzed nitration consumes the amine rapidly, the acetylation will correspondingly be decreased. A separate experiment demonstrates that dibutylacetamide is not convertible to nitramine under these reaction conditions. Finally it is found that when the reaction is carried out in butyric anhydride (Expt. 21) instead of acetic anhydride the yield of dibutylbutyramide is about that expected for the acetamide under the same reaction conditions. Surprisingly the nitrosamine yield is high and so is the nitramine yield. However, the experiment is not comparable with others because the addition time is only half that used for the other experiments.

Inspection of Table I reveals that complete recovery of the amine either of itself or as its reaction products is not quite complete. A search for other products has yielded about 2 mole % as monobutylamine and about 3.5% as butylaldehyde.



Diisobutylamine is more strongly proton-attracting than di-*n*-butylamine, but since both contain primary alkyl groups their behavior during nitration ought to be similar. This is approximately true, although the yield of acetamide was almost double the low (17%) yield of nitramine which was obtained from the nitrate salt and 4 mole % of zinc chloride in acetic anhydride. The modest amount of catalyst used might be expected to induce a low nitrosamine yield; none was detected although it undoubtedly was present in small amount.

Dicyclohexylamine in acetic acid was also strongly proton-attracting among the amines studied in this series. This agrees with the reported base strength determined in ethanol (14, 15). It differs from the amines previously nitrated in that its alkyl groups are secondary rather than primary. This difference must account for the fact that its nitration is more difficult than the nitration of di-normal and diisobutylamines, between which it lies in relative proton-accepting ability (1, 9). No recognizable product except dicyclohexylammonium nitrate (22%) and dicyclohexylnitrosamine (68%) could be separated when 4 to 10 mole % of hydrochloride was used as a catalyst, so dicyclohexylamine hydrochloride itself was treated with nitric acid and acetic anhydride at 25° C. over 30 hr. The product was a complex mixture containing dicyclohexylnitrosamine and nitramine but no dicyclohexylacetamide (1, 9). Since the properties of dicyclohexylacetamide are very similar to those of the known nitrosamine (25) and to the nitramine which we obtained, the absence of acetamide could not be ascertained by crystallization procedures. We found, however, that dicyclohexylacetamide was adsorbed on silicic acid and hence was amenable to chromatographic separation. The detail of this separation is shown in Table II. Since the dicyclohexylnitrosamine and nitramine were not separable in the silicic acid column their percentages were ascertained by thermal analysis. The table represents in Expt. 1 a trial mixture of the acetamide, nitrosamine, and nitramine. This shows that a fairly accurate estimate could be made of the proportions of these several compounds in a mixture. Expts. 2, 3, and 4 were then carried out on aliquots *A* (withdrawn after five hours' reaction time), *B* (withdrawn after 22 hr.), and *C*, the remainder of the reaction mixture after final heating to 40° C. This examination demonstrated definitely that no dicyclohexylacetamide was formed, since the low melting fractions which adsorbed at the top of the column were carefully examined and found to contain none of this compound. The apparent decrease in nitramine and nitrosamine yields is of course owing to the increase in amount of low melting impurity in the aliquot as the age of the reaction increased. Actually the ratio between nitramine and nitrosamine yield became constant at about 10 : 1 after five hours at 25° C. The final yields of these two compounds were, respectively, 50 and 5% of the theoretical amount.

Diisopropylamine is the most strongly proton-attracting amine of all those examined in this series. It also possesses secondary rather than primary alkyl groups. Like dicyclohexylamine it might therefore be expected to



TABLE II  
CHROMATOGRAPHY OF DICYCLOHEXYLAMINE

## NITRATION PRODUCT

Column: 2 : 1 or 4 : 1 Silicic acid - Celite 20  $\times$  180 mm.

Prewash: 1 Vml. of ether, 2 Vml. petroleum ether (b.p. 60° to 70° C.), where Vml. indicates volume of solvent in ml. required to wet the column completely; developer, petroleum ether (b.p. 60° to 70° C.).

Expt. No.	Sample	Wt., mgm.	Developer, Vml.	Column section			Analysis		
				Length from top, mm.	Eluate, % total	Eluate m.p., °C.	Acetamide, %	Nitrosamine, %	Nitramine, %
1	(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NAc (C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NNO (C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NNO <sub>2</sub>	30	2	40	26	98-100	26	29	33
		30		105	17	104			
		30		160	45	107			
2	Crude A (5 hr.)	300	2.5	80	3	—	None	8	78
				160	12	115			
				180 + <sup>2</sup>	74	130.5			
3	Crude B (22 hr.)	300	2	60	11	78 <sup>1</sup>	None	7.5	71
				180	36	125			
				180 + <sup>2</sup>	42	132			
4	Crude C (40°)	300	2.2	50	9	76 <sup>1</sup>	None	5.5	58
				135	19	83 <sup>1</sup>			
				180	29	126			
				180 + <sup>2</sup>	34	133			

<sup>1</sup> Not acetamide.

<sup>2</sup> These fractions were recovered from developer which had passed through the column.

nitrate with difficulty, and this was found to be the fact. When the nitration was attempted with a 4% molar equivalent of amine hydrochloride as catalyst, at least 60% of amine could be recovered as the nitrate salt. A small yield of the known diisopropylnitrosamine was also found, but none of the nitramine was produced.

These results indicated that more drastic treatment was required. Accordingly a full equivalent of hydrogen chloride was used (as the amine salt) together with a corresponding excess of nitric acid and acetic anhydride. Under these conditions nitramine and nitrosamine were produced in molar quantities that were approximately equal. The separation of the two was difficult, and only 10% yields of each pure compound were obtained. A rough estimate from the crystallization procedure would indicate that about 30% of each was in the original crude product.

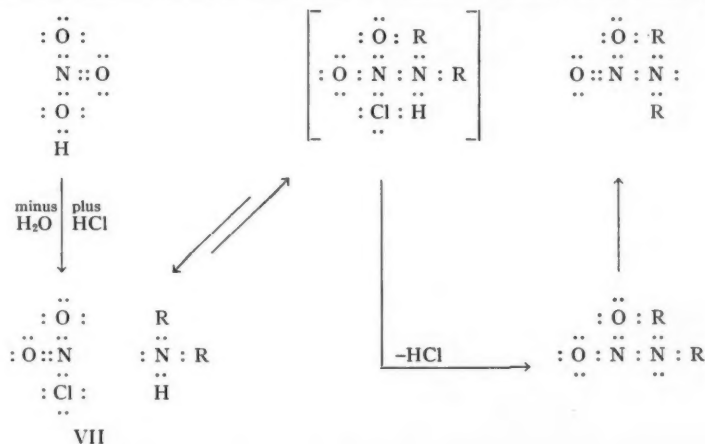
Both the nitrosamine (25) and the nitramine (24) have previously been reported. The properties of the nitrosamine conformed with those reported by Van der Zande. Our nitramine, however, was solid while that reported by Thomas was a liquid. Our compound was stable toward heat, oxidizing agents, and 50% sulphuric acid, whereas Thomas' oil was comparatively

unstable under these conditions. By analogy with the pair of isomers we obtained by treatment of *n*-butyl iodide with the potassium salt of *n*-butyl-nitramine we believe Thomas' compound to be diisopropylisonitramine while ours is the true nitramine.

A significant feature of this nitration, like that of dicyclohexylamine, was the complete absence of any material resembling diisopropylacetamide among the products. Since neither of the amines which contain secondary alkyl groups is converted to acetamide during the nitration, one is inclined to the belief that such acetylation is hindered by steric effects. Steric hindrance may also account for the difficulty in nitration which would not have been predicted on the basis of proton-attracting ability of either dicyclohexylamine or diisopropylamine.

It may be seen from the nitration of this array of amines that the proton-attracting tendency is the principal factor in the formation of the nitramine although steric effects likewise are involved. By-product formation increases as the rate of nitramine formation slows down. None of the by-products are convertible to nitramine under the reaction conditions. The formation of one of these by-products, the dialkylacetamide, is independent of the chloride catalyst, but the extent of formation of the other, dialkylnitrosamine, depends directly on the amount of catalyst used in the reaction. Finally, since the yield of nitramine is dependent on the proton-attracting ability of the amine as well as on the chloride catalyst it is probable that the chloride acts in some way either to weaken the proton attraction of the amine or to strengthen the electron attraction of nitric acid. Either effect would tend to create the covalent nitrogen-nitrogen bond in the resulting nitramine.

The alternative possibility that hydrogen chloride may increase the electron-accepting propensity of nitric acid at the nitrogen atom suggests that nitryl chloride, VII, might be an intermediate in the reaction because its electron-attracting chlorine atom would create a greater deficiency at the nitrogen of



the nitric acid than would the hydroxyl group. Since there is still some doubt whether nitril chloride is an isolable compound, a test of this theory did not seem worth while with the substance in question. One might however expect nitracidium perchlorate to behave in the same way. Accordingly an attempt was made to nitrate di-*n*-butylamine with this reagent, but without success. This failure indicated, as well, that perchloric acid was not a catalyst in the nitration reaction. An attempted nitration of dibutylammonium nitrate in acetic anhydride containing perchloric acid demonstrated that it would indeed not replace hydrochloric acid as the catalyst.

### Experimental\*

#### *Nitrimino-bis-acetonitrile*

To a stirred solution of 108 gm. (1.06 moles) of acetic anhydride and 3.8 gm. (0.052 mole) of 99% nitric acid (prepared at 0° C.) was added proportionately at 10° to 15° C. 16.7 gm. (0.266 mole) of nitric acid and 22 gm. (0.212 mole) of imino-*bis*-acetonitrile (m.p. 77° C.) (8). A white precipitate formed on completion of the addition, which required 25 min. The reaction mixture was then heated to 40° C. for 10 min., cooled to 5° C., and diluted to 1.5 liters with ice and water. Filtration yielded a water-washed product weighing 27.7 gm., a 93.4% molar yield. This product melted at 94.5° to 95.5° C.

When this procedure was varied by adding all the nitric acid initially to the acetic anhydride, the yield of nitrimine was lower (86.5%) but the product melted at 95.5° to 96.5° C. When the imino-*bis*-acetonitrile contained hexamine the yield and quality of product were very poor.

Nitrimino-*bis*-acetonitrile was purified by solution in acetone (1 gm. per 3 cc. at 25° C.) and dilution of this filtered solution with 10 volumes of water. The purified material melted at 96° to 97° C., somewhat lower than that reported previously (11) but a repetition of these authors' preparation (yield 60%) gave material which also melted at 96° to 97° C. when crystallized from benzene.

#### *Imino-bis-methylacetonitrile*

The imino-*bis*-methylacetonitrile used in this work was prepared according to Dubsky (5). The crude product was crystallized from ether to give a 39% yield of the solid diastereomer, m.p. 68° C. The filtrate was evaporated and then repeatedly molecularly distilled at 70° C., thrice at 60°, 50°, and 30° C. until, on completion of the final distillation, no crystals of the 68° C. diastereomer sublimed on to the condenser. This final distillate seems to be the other (liquid) diastereomer which is almost free from the less volatile (solid) diastereomer. This oil,  $n_D^{25}$  1.4378, was analyzed. Calc. for  $C_6H_9N_3$ : C, 58.5; H, 7.37; N, 34.1%. Found: C, 58.5; H, 7.43; N, 33.6%.

\* All melting points have been corrected against reliable standards.

*Nitrimino-bis-methylacetoneitrile**A. From Solid Diastereomer*

To 5.1 gm. (0.05 mole) of acetic anhydride was added 0.05 cc. (0.0012 mole) of 99% nitric acid at 5° C. This solution was stirred at 15° C. while 0.95 gm. (0.0145 mole) of 99% nitric acid and 1.23 gm. (0.01 mole) of imino-bis-methylacetoneitrile (m.p. 68° C.) were added proportionately over 30 min. After stirring this mixture for an additional four hours at 25° C. the acetic acid and excess anhydride were evaporated under 3 mm. pressure.<sup>3</sup> The crystalline residue was washed with 25 cc. ether to yield 1.56 gm. (93.1% of theory) melting at 94° to 95.2° C. Further crops of 5.1% (m.p. 93° to 94° C.) and 0.5% (m.p. 88° to 90° C.) were obtained from the ether used for washing.

When this procedure was repeated with inclusion of chloride catalyst the yield and quality of product were essentially the same.

*B. From Liquid Diastereomer*

The procedure outlined in *A* was repeated with the liquid diastereomer to yield 1.74 gm. (96.3% of theory) of crude nitrimine melting at 94.5° to 96.5° C. This was crystallized from ethanol to melt at 100.7° to 101.5° C. In addition to this 96% yield of high melting diastereomeric nitrimine, the final ether washings yielded 0.017 gm. of lower melting material which represented a 1.88% yield of lower melting diastereomer, m.p. 86° to 95° C. Crystallization from ethanol raised this melting point to 94° to 95° C. A mixed melting point with the product obtained from the 68° C. diastereomer was not lowered, but admixture with the diastereomer melting at 100.7° to 101.5° C. was lowered to 68° C.

*Nitrimino-bis-dimethylacetoneitrile*

The imino-bis-dimethylacetoneitrile used in this work was prepared by the method of Dubsky (6) in 10% yield. It melted at 47.8° to 48.0° C. A solution of 2.55 gm. (0.025 mole) of acetic anhydride and 0.02 cc. (5% of total) of 100% nitric acid was prepared at 0° C. and stirred at 15° C., while 0.69 gm. (0.0046 mole) of amine and 0.30 cc. (total is 0.0075 mole) of 100% nitric acid were added proportionately over 30 min. Five minutes after addition was started a white precipitate appeared. The mixture was heated to 25° C. after completion of addition and maintained for four hours. After 20 min. at 25° C. the precipitate redissolved. The reaction liquor was finally evaporated to dryness at 10 to 15 mm. The residue was dissolved in ether; evaporation left 0.9 gm. (quantitative yield) of nitrimine melting at 52° to 53° C. (soft 51° C.).

When this experiment was repeated using the amine hydrochloride (prepared from hydrogen chloride and amine in ether, m.p. 90° to 95° C., crystallized from ethanol-ether to melt at 100° to 101° C.) as catalyst, the yield and quality were identical. On the other hand, when 2 mole % of zinc chloride was used as the catalyst the yield of nitrimine was only 50% (m.p. 49° to 53° C.) and ammonium nitrate, m.p. 167° to 168°, also was produced in 15 to 20% yield

on a 2 : 1 basis. Since the nitramine could be recovered almost quantitatively from a mixture of acetic anhydride, 100% nitric acid, and zinc chloride in the same proportion and under the same reaction conditions it would seem evident that zinc salt prevented the nitration through destruction of the amine nitrate.

The nitrimine is quite soluble in most solvents except water and petroleum ether. It was twice purified by dissolving it in twice its weight of acetone and then diluting with five times the weight of water. Further threefold crystallization from 50 volumes of petroleum ether (b.p. 60° to 70° C.) and then from absolute ethyl ether yielded a purified specimen melting at 55.0° C. Calc. for  $C_8H_{12}N_4O_2$ : C, 49.0; H, 6.18; N, 28.6%. Found: C, 48.7; H, 6.18; N, 28.8%.

#### *Imino-bis-propionitrile (2)*

To 995 gm. (18.7 moles) of stirred acrylonitrile maintained at 20° C. was added 660 cc. (10.5 moles) of 28% aqueous ammonia. After 15 hr., this crude mixture was at first distilled under vacuum to remove water. The residue was then distilled under 10 to 11 mm. to remove a first fraction, from 1 to 3% of the total boiling below 190° C.,  $n_D^{20}$  1.4600. The remainder then was distilled at 158-160° C. (3 mm.) to yield 1060 gm.,  $n_D^{20}$  1.4627, of good imino-bis-propionitrile or 90% of the theoretical yield. The melting point of the oil is -6° to -4.8° C.

#### *Imino-bis-propionitrile Nitrate*

Forty cubic centimeters of crude imino-bis-propionitrile was stripped of its volatile component by passage through a flash distillation apparatus at 50° C. (15 mm.). The residue was dissolved in 200 cc. acetic acid. Nitric acid (99%) in 2 volumes of acetic acid was added to this at 20° C. until the pH of a test sample in water was 2. The precipitated salt was filtered, washed with 20 cc. acetic acid, and air-dried. This product still contained acetic acid, and its melting point (122° to 130° C.) was consequently poor but it was completely satisfactory for the nitration described below. The yield was 87% of that expected from the acrylonitrile used for the crude imino-bis-propionitrile.

The crude salt could be purified by solution in 70% ethanol at 60° C. Cooling to 10° C. gave crystals which when washed with ether and dried (with difficulty) in vacuum melted at 132.6° to 133.2° C. The pure dry material is not deliquescent and is stable at 50° C. for at least four days, but damp salt picks up additional moisture from the air and gradually decomposes.

#### *Imino-bis-propionitrile Hydrochloride*

A stirred solution of 25 gm. (0.2 mole) of imino-bis-propionitrile in 200 cc. of 95% ethanol was chilled to 0° C. while 17 cc. (0.2 mole) of concentrated hydrochloric acid was slowly added. A 96% yield of the hydrochloride precipitated, m.p. 148.5° to 150.4° C.

*Nitrimino-bis-propionitrile**A. From Imino-bis-propionitrile Nitrate*

To 0.58 gm. (0.006 mole) of 37% hydrochloric acid was added 36.2 gm. (0.32 mole) of 92% acetic anhydride. This solution was stirred at 15° C. while 33.5 gm. (0.18 mole) of imino-bis-propionitrile nitrate and 2.3 gm. (0.036 mole) of 99% nitric acid were added proportionately over 30 min. The salt dissolved but a precipitate reappeared. After two hours' stirring the suspension was cooled to 0° C. and diluted with 10 cc. of water. Filtration of the cold suspension yielded 26.1 gm., m.p. 56° to 56.5° C. Further dilution of the filtrate with 10 cc. more water yielded 2.9 gm. melting at 53.5° to 55.5° C. The total crude yield was 96%.

*B. From Imino-bis-propionitrile*

To 2170 gm. of 95% acetic anhydride at 3° C. was added with stirring 18.9 gm. (0.3 mole, 5% of the total) of 99.3% nitric acid and then 19.6 gm. (0.123 mole) of imino-bis-propionitrile hydrochloride. The temperature was raised to 15° C. and, over 50 min., 506 gm. (4.1 moles) of bis-iminopropionitrile and 253 cc. (6.0 moles) of 99.3% nitric acid were added proportionately to the stirred solution. The temperature was then raised to 25° C. and maintained there for six hours. The reaction mixture was subsequently distilled at 40° C. (14 mm.) to remove acetic and excess nitric acids. The residue was treated with 270 cc. water to hydrolyze the remaining anhydride and the distillation was resumed. The residue was then treated with 1 liter of water and the precipitated solid, 476 gm., was filtered off. It melted at 53.8° to 55.8° C. and represented 71% of the theoretical yield. Further evaporation of the filtrate yielded an unidentified oil.

*C. Reaction Without Catalyst*

When procedure *B* was carried out without addition of chloride catalyst, 85% of the amine was recovered as its nitrate salt and no nitramine could be detected.

*D. Purification*

A filtered solution of 380 gm. crude nitramine (m.p. 53.8° to 55.8° C.) in 400 cc. acetone was cooled to 10° C. and 100 cc. of water was added. The solution became cloudy; it was stirred until crystallization was complete. An 85% recovery of nitrimino-bis-propionitrile was thus effected after washing with water-acetone. It melted at 55.7° to 56.7° C. This melting point was not raised by further recrystallization. Calc. for  $C_6H_8N_4O_2$ : C, 42.9; H, 4.76; N, 33.3%. Found: C, 43.1; H, 4.85; N, 33.0%.

*Imino-bis-propionic Acid Nitrate*

A solution of 12.3 gm. (0.1 mole) of imino-bis-propionitrile in 45 cc. (0.7 mole) of 70% nitric acid was prepared with stirring at 0° C. and then boiled under reflux for five minutes. The cooled solution was then diluted with 75 cc. of acetone. After 12 hr. at 0° C., 12.5 to 14.4 gm. of ammonium nitrate was filtered off (67 to 77% of the expected amount). Further cooling of the



filtrate to  $-75^{\circ}\text{C}$ . yielded 19.4 gm. of crude nitrate salt melting at  $88^{\circ}$  to  $98^{\circ}\text{C}$ . A further crop of 3.35 gm., m.p.  $85^{\circ}$  to  $95^{\circ}\text{C}$ ., was obtained by dilution of the filtrate with 100 cc. ether. This salt probably contained  $\beta$ -alanine, since it evolved nitrogen on treatment with nitrous acid. It could be crystallized from methanol and reboiled with 70% nitric acid to melt at  $103^{\circ}$  to  $105^{\circ}\text{C}$ . It resisted further purification either as the salt (calc. N, 12.5; found, 15.2) or as the free acid (calc. N, 8.69; found, 9.49).

#### *$\beta$ -Nitrimino-bis-propionic Acid*

To 5.1 gm. (0.05 mole) of acetic anhydride was first added 0.05 cc. of 99% nitric acid at  $5^{\circ}\text{C}$ ., followed by 0.04 gm. (0.0003 mole) of zinc chloride. To this mixture at  $15^{\circ}\text{C}$ . was added 2.24 gm. (0.01 mole) of the impure nitrate salt of  $\beta$ -imino-bis-propionic acid (calc. N, 12.5; found, 15.2) together with an additional 0.16 cc. of nitric acid (total 0.005 mole). After 30 min. the solution was clear. Tests for hypochlorous acid were positive over the next 210 min. after which the whole was evaporated under reduced pressure. The syrupy residue was dissolved in acetone and this solution chilled to remove 0.15 gm. of a zinc salt. Evaporation of the filtrate left 1.55 gm. of crude  $\beta$ -nitrimino-bis-propionic acid, m.p.  $152^{\circ}$  to  $158^{\circ}\text{C}$ . This was crystallized from acetic acid (the crystals being ground in ether during a subsequent wash) and then from ethyl acetate, after which it melted at  $162^{\circ}$  to  $162.5^{\circ}\text{C}$ . If the original nitrate salt had been pure, the nitrimine yield would have been 75% of theoretical. Calc. for  $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_6$ : C, 34.9; H, 4.89; N, 13.6%. Found: C, 34.3; H, 5.02; N, 13.5%.

A repetition of this procedure wherein the zinc chloride was left out gave a 61.6% recovery (1.38 gm.) of the original nitrate salt, m.p.  $95^{\circ}$  to  $102^{\circ}\text{C}$ . This salt was insoluble in acetone. Evaporation of the acetone used to wash it yielded an oil from which no nitramine could be isolated.

#### *Nitromorpholine*

A solution of morpholine nitrate in acetic acid was prepared by adding 698 cc. (8 moles) of morpholine (b.p.  $126^{\circ}$  to  $130^{\circ}\text{C}$ .) to 3150 cc. (55 moles) of stirred acetic acid over 10 min. with water cooling of the 2 gal. stainless steel kettle to maintain the solution at  $30^{\circ}\text{C}$ . To this was added with stirring over nine minutes a solution at  $25^{\circ}\text{C}$ . of 371 cc. (8.6 moles) of 99% nitric acid in 375 cc. (6.5 moles) of acetic acid. The temperature could be maintained at  $30^{\circ}\text{C}$ . by water cooling. The resulting solution of morpholine nitrate in acetic acid was maintained at  $45^{\circ}\text{C}$ . (in order to avoid crystallization) in the vessel from which it was added to the anhydride-catalyst solution.

The latter solution was prepared in 20 min. in a stirred 2 gal. stainless steel vessel from 830 cc. (8.8 moles) of acetic anhydride and 43.6 gm. (0.32 mole) of zinc chloride. This stirred solution was maintained at  $25^{\circ}\text{C}$ . by water cooling while the morpholine nitrate solution was added over 13 to 17 min. at 300 cc. per min. Fifteen minutes after addition was complete, the temperature was raised to  $55^{\circ}\text{C}$ . and maintained for 15 min. The acetic acid was then removed under 12 to 20 mm. pressure.



Four liters of hot water was added to the residue and steam was bubbled through for 15 min. The residual liquor was then filtered and cooled to 10° C. with stirring. The crystalline product was filtered and dried in an air draft at 42° C. It weighed 686 gm. or 65% of theoretical. The product melted at 53.0° to 53.8° C. and showed an Abel Heat Test of 8 min. at 100° C. A 5 gm. sample in the vacuum stability test gave a maximum of 2.6 cc. of gas in 45 hr. at 100° C. The melting point was not raised by crystallization from ethanol.

The solubility of nitromorpholine in water is 0.15 gm. per cc. at 100° C. and 0.04 gm. per cc. at 10° C. The water used for purification therefore contained considerable product. In subsequent experiments this purification water was re-used to raise the yield to 93% of theoretical without lowering the quality of product.

Nitromorpholine gives a reliable positive Franchimont test only if water is added with acetic acid. The compound is stable at 100° C. and cannot be detonated by ordinary impact. Calc. for  $C_4H_8N_2O_3$ : C, 36.3; H, 6.10; N, 21.2%. Found: C, 36.2; H, 5.85; N, 21.4%.

The yield of nitromorpholine was 93% of theoretical when 0.16 mole of morpholine hydrochloride was treated with 0.79 mole of nitric acid and 0.79 mole of acetic anhydride at 5° to 7° C. over 14 min. In this case the nitromorpholine dissolved in the water was recovered by extraction with chloroform.

#### *Diethylnitramine*

A mixture of 136 gm. (1 mole) of diethylammonium nitrate, 3.15 gm. (0.05 mole) of 100% nitric acid, 5.44 gm. (0.04 mole) of zinc chloride, and 255 gm. (2.5 moles) of acetic anhydride was heated two and one-half hours at 50° to 55° C., then poured into ice. The mixture was neutralized with aqueous sodium carbonate and extracted with ether. The ether solution, dried with magnesium sulphate, was distilled to yield a small fraction boiling up to 174° C., mostly nitrosamine, then a fraction boiling principally at 185° to 190° C., wt. 9.2 gm. or 8% of the theoretical conversion to diethylacetamide. The third fraction boiled at 203° to 205° C. and weighed 71 gm. This represents 60% of the theoretical conversion to diethylnitramine.

#### *Diethylacetamide*

Into 38.7 gm. (0.38 mole) of stirred acetic anhydride containing 1.36 gm. (0.01 mole) of anhydrous zinc chloride and maintained at 10° to 15° C. were added, over 45 min., 25 gm. (0.34 mole) of diethylamine and 23.9 gm. (0.37 mole) of 98.2% nitric acid at proportionate rates. The mixture was then heated to 40° C. for 90 min. and poured into 100 cc. of water. After neutralization with sodium carbonate the liquor was exhaustively extracted with 250 cc. of ether. This solution was dried and distilled to yield 2.2 gm. of impure diethylnitrosamine (6% of theoretical) boiling at 174° to 184° C. and 13 gm. of diethylacetamide (34% of theoretical) boiling at 185° to 186° C. There was no higher boiling fraction of diethylnitramine.

*Diisopropylnitramine and Nitrosamine**A. From Diisopropylamine*

When diisopropylamine (b.p. 83.5° to 84° C. (755 mm.)) was added proportionately and equivalently to acetic anhydride containing 0.1 equivalent each of the hydrochloride salt and absolute nitric acid at 15° C., the recovery of amine (as the nitrate salt) after six hours was 60%. A 13% yield of diisopropylnitrosamine (17, 18) b.p. 76° to 81° C. (14 mm.), m.p. 42° to 47° C., was also obtained, but no diisopropylnitramine could be found.

*B. From Diisopropylammonium Chloride*

Diisopropylammonium chloride (12.87 gm., 0.095 mole) was mixed with a solution of 11.5 cc. (0.286 mole) of 98% nitric acid and 77.2 cc. (0.810 mole) of acetic anhydride at -50° C. This slurry was warmed slowly to 20° C. An exothermic reaction took place with evolution of nitrogen oxides which raised the temperature to 30° C. The reaction mixture was heated to 40° C. for 45 min., then diluted with 8 gm. of water. Distillation at 14 mm. removed the acetic acid and anhydride. The residue was dissolved in ether and this solution washed with dilute nitric acid, dried with magnesium sulphate, and distilled to give 8 gm. of semisolid oil boiling from 53° to 85° C. (14 mm.). This was repeatedly extracted with concentrated hydrochloric acid to remove nitrosamine, which was regenerated from the acid solution by neutralization and crystallized from water to yield 1.25 gm. (10% of theoretical) of diisopropylnitrosamine, m.p. 42° to 46° C. The oil which was insoluble in concentrated hydrochloric acid still contained nitrosamine, but it was crystallized from 85% ethanol to yield 1.39 gm. (10% of theoretical) of diisopropylnitramine melting at 105° to 107° C. Owing to the wasteful separation neither of these yields should be considered as representative. The yields of the two products are estimated from the crystallization procedure each to be about 30% of theoretical.

Further crystallization from acetic acid and 85% ethanol raised the melting point of the nitramine to 108.0° to 108.5° C. This compound would not give a Franchimont test although it gave a strong Liebermann nitrosamine test. It was extremely resistant toward oxidizing agents, but reduction with zinc and acetic acid yielded, after distillation of the resulting reaction mixture with alkali, a strong positive test for hydrazine. This test was obtained with sodium pentacyanamine ferroate. Molecular weight determinations by the Rast method in camphor gave high values (230) but the ebullioscopic method (Richter) gave values of 128 in acetone and 138 in chloroform (calc. 146). Calc. for  $C_6H_{14}N_2O_2$ : C, 49.3; H, 9.66; N, 19.2%. Found: C, 49.3; H, 9.82; N, 18.6%.

A comparison of this compound with that reported by Thomas (24) shows that the 108° C. compound is much more stable toward 50% sulphuric acid than Thomas' oil. The latter is probably the isonitramine.

*n*-Dibutylacetamide*A. Preparation in Presence of a Chloride*

Glacial acetic acid, 6.0 gm. (0.10 mole), was mixed with 15.3 gm. (0.15 mole) of acetic anhydride and 0.54 gm. (0.004 mole) of zinc chloride. The reagents were protected against atmospheric moisture, cooled, and stirred while 12.9 gm. (0.10 mole) of di-*n*-butylamine was dropped in from a burette. This addition lasted 17 min. Meanwhile the temperature was held at 15° to 17° C. The products were raised to 55° C. for 20 min. before being diluted with 48 cc. of water. The diluted solution was neutralized with sodium carbonate. The upper layer, which separated, was taken up in ether and the aqueous layer extracted four times (a total of 150 cc. of ether). The ethereal solution was dried and the solvent removed by flash distillation. The residual liquid was distilled at 117° to 121° C. (8 mm.). The distillate weighed 14.70 gm. This corresponded to 86.1% of the theoretical yield of di-*n*-butylacetamide.

When 0.0013 mole of dibutylammonium nitrate was treated with 0.7 mole of acetic anhydride for 24 hr. at 0° C., no acetamide was formed, but 8.7% of the amine was recovered. On the other hand dibutylammonium chloride under the same conditions gave a 15% yield of dibutylacetamide after one hour at 100° C. The yield was 92% of theoretical.

*B. Preparation Without Chloride*

This reaction was carried out exactly as that just described, but no zinc chloride was employed. Times and temperature of the first reaction were reproduced exactly. A yield of 14.85 gm. (87% of theoretical) of di-*n*-butylacetamide, b.p. 117° to 120° C. (8 mm.), was obtained. Calc. for  $C_{10}H_{21}NO$ : C, 70.1; H, 12.40; N, 8.19%. Found: C, 70.6; H, 12.65; N, 8.50%.

*C. Attempted Conversion to Di-n-butylnitramine*

Di-*n*-butylacetamide, 7.9 gm. (0.05 mole) was added to 9.12 cc. (0.15 mole) of glacial acetic acid, 6.4 cc. (0.15 mole) of 98% nitric acid, 6.8 gm. (0.05 mole) zinc chloride, and 1.0 cc. (0.01 mole) acetic anhydride. The whole was heated at 40° to 50° C. for 24 hr. The products were poured into 75 cc. water and extracted four times with ether. The ethereal solution was washed with 5% sodium hydroxide until neutral, dried, and flash distilled. The residue, upon distillation, gave a fraction of 0.87 gm., b.p. 65° to 112° C. (10 mm.), and the remaining 5.54 gm. boiled at 114° to 117° C. (8 to 9 mm.). The lower boiling fraction smelled like an ester. The higher boiling portion gave no Franchimont test for a nitramine (10). It was not decomposed upon heating in a refluxing solution of acetic acid and sulphuric acid. The recovery was 70% of the original di-*n*-butylacetamide. A similar experiment was carried out with diethylacetamide. No nitramine was obtained.

*Di-n-butylnitramine**A. From n-Butylnitramine and n-Butyl Iodide*

To a solution of 22.4 gm. (0.4 mole) of potassium hydroxide in 250 cc. of 95% ethanol was added 47.2 gm. (0.4 mole) of monobutylnitramine (16),

b.p. 112.3° C. at 11 mm., and 74 gm. (0.4 mole) of *n*-butyl iodide. The resulting sludge was stirred for 12 hr. at 25° C. and then refluxed for 24 hr. during which time the potassium iodide separated out on the side of the flask. The ethanol was then removed by distillation and the oily residue diluted with 300 cc. (0.4 mole) of aqueous potassium hydroxide. The mixture was extracted with four 100 cc. portions of ether. The extracts gave 42 gm. of liquid, b.p. 88° to 130.3° C. (11 mm.). Subsequent fractional distillation of this liquid through a column of the Vigreux type gave two compounds. The low boiling, watery liquid (dibutylisonitramine) weighed 16.5 gm. (24% of theory), b.p. 97° to 98.7° C. (11 mm.);  $d_4^{25}$  0.9255;  $n_D^{25}$  1.4393. It did not crystallize on cooling to -70° C., was unstable in cold 70% sulphuric acid, and gave a negative Franchimont nitramine test and a negative Liebermann nitrosamine test. Molecular refraction: calc.  $MR_D^{25}$  49.15; found, 49.50 (*L.L.*). Calc. for  $C_8H_{18}N_2O_2$ : C, 52.2; H, 10.34; N, 16.1%. Found: C, 52.2; H, 10.35; N, 16.1%.

The higher boiling fraction (di-*n*-butylnitramine) weighed 22 gm. (32% of theory), b.p. 127° to 130.3° C. (11 mm.), with the main fraction boiling at 129° to 130° C. (11 mm.);  $n_D^{25}$  1.4557;  $d_4^{25}$  0.9616. This colorless liquid crystallized easily on cooling, m.p. -22° C. The nitramine is a colorless, oily liquid which is unstable in boiling 70% sulphuric acid, but much more stable than the isonitramine. It gave a positive Franchimont nitramine test and a positive Liebermann nitrosamine test. Molecular refraction: calc.  $MR_D^{25}$  49.15; found, 49.23 (*L.L.*). Calc. for  $C_8H_{18}N_2O_2$ : C, 55.2; H, 10.34; N, 16.1%. Found: C, 55.4; H, 10.35; N, 16.1%.

The aqueous alkaline residue from the ether extractions was acidified with sulphuric acid and 12.2 gm. of monobutylnitramine (26% of original) was recovered unchanged.

When 0.648 gm. (0.00372 mole) of di-*n*-butylnitramine, b.p. 129° to 130° C. (11 mm.), was refluxed for two hours in a solution of 12.5 cc. of 70% sulphuric acid in 12.5 cc. of acetic acid, 0.00245 mole of gas was collected after it was bubbled through a column of 40% aqueous potassium hydroxide. The gas was found to contain no appreciable amount of nitric oxide and is believed to be nitrous oxide (66% of theory, 1 : 1 mole). Di-*n*-butylisonitramine on similar treatment gave 2.1 moles of gas per mole of sample.

### B. By Nitration

The acetic anhydride, together with the catalyst and an equivalent amount of nitric acid (and acetic acid in many experiments), was stirred while the nitric acid and amine were added proportionately over two hours. Cooling was necessary to maintain the desired reaction temperature during this addition, but a thermostat adequately maintained this temperature during the remainder of the reaction period. After completion of the reaction, the excess anhydride was hydrolyzed with water and the total acetic acid was then distilled under 12 to 15 mm. pressure. This acetic acid distillate was found to contain at least 0.2% of butyl acetate, b.p. 125° C. It also contained

butyraldehyde. This was isolated by addition of 15 ml. of 30% alkali to neutralize strong acid and then 10 mole % of phenylhydrazine. After 10 hr. the acetic acid was evaporated under 15 mm. and the residue taken up in water and extracted thoroughly with benzene. The benzene solution, dried with magnesium sulphate, was distilled at 80 mm. to collect the fraction of butyraldehyde phenylhydrazone boiling at 185° to 195° C. The yield was 3.5 mole % of the original dibutylamine. The residue remaining after distillation of the acetic acid was taken up in water. An aliquot was removed, extracted with ether, then cooked with standard alkali to remove the amine, and titrated with standard acid to determine the residual nitric acid. The remainder of the residual reaction mixture was acidified to an acid concentration not exceeding 2%, then extracted with ether. The remaining aqueous solution was made alkaline and steam distilled to estimate amine recovery, either by actual isolation, or by titration. When the isolated amine was distilled, about 2 mole % of monobutylamine was obtained, boiling at 75° to 80° C. This was identified as its *p*-bromobenzenesulphonamide, m.p. 59° to 60° C. The ether solution was separated into the three main reaction products as described below.

*Separation of Dibutylacetamide from Dibutylnitrosamine-dibutylnitramine*

Fifteen grams of a mixture containing equal weights of the dibutylacetamide, nitrosamine, and nitramine was diluted with three volumes of ether. This solution was extracted eight times with a total of 400 ml. of 12% hydrochloric acid. A test portion of the final extract showed no precipitation of dibutylacetamide when it was made alkaline. The combined acid extracts were made alkaline with 50% aqueous sodium hydroxide to pH 10 and then extracted with four 75 ml. portions of ether. The dried ether extract gave 4.9 gm. of dibutylacetamide, boiling from 136° to 138° C. (22 mm.) (recovery 98%).

*Separation of Dibutylnitramine from the Nitramine-nitrosamine Mixture*

*Method A*

Evaporation of the ether solution which was extracted with 12% hydrochloric acid as described above left 9.8 gm. of oil;  $n_D^{20}$  1.4522. This was extracted with three successive 3 ml. portions of concentrated hydrochloric acid. The acid extract was diluted with water and neutralized with aqueous sodium carbonate to pH 10. Three extractions with a total of 25 ml. of ether removed the nitrosamine; the solution was dried with Drierite and evaporated to leave 4.55 gm.,  $n_D^{20}$  1.4468, or 93% of the nitrosamine originally added. Purification by distillation at 113° to 116° C. (14 mm.) or 108° to 109° C. (10 mm.) gave a colorless liquid;  $n_D^{25}$  1.4457.

The oil remaining after the extraction with concentrated hydrochloric acid was diluted with ether, washed with water and aqueous sodium carbonate solution until neutral, then dried over Drierite, and the ether evaporated to leave 5.25 gm. as nitramine,  $n_D^{20}$  1.4560, or 106% of that originally introduced.



### Method B

The same mixture used in Method A (9.8 gm. of oil) was treated with 35.5 gm. (0.358 mole) of cuprous chloride and 196 ml. (1.9 moles) of concentrated hydrochloric acid and warmed to 55° C. When vigorous gas evolution subsided, the mixture was heated to 100° C. for 15 min. (or until cessation of gas evolution) then diluted with three volumes of water and steam distilled. About 1 liter of distillate was ether-extracted to yield, after evaporation, 5.1 gm. of dibutylamine ( $n_D^{20}$  1.4540) or 102% of that originally present.\*

The residual steam distillation liquors were made strongly alkaline. Steam distillation was resumed until no more dibutylamine distilled (500 ml.). Titration with standard acid accounted for 92% of the amine expected by decomposition of the nitrosamine.

### Catalytic Effect of Nitracidium Perchlorate

The nitracidium perchlorate (14, 15) was prepared from 45 gm. (0.76 mole) of 106% nitric acid ( $\text{HNO}_3 + \text{N}_2\text{O}_5$ ) cooled to -8° C., to which 9.2 gm. (0.055 mole) of 69% perchloric acid was added slowly. The white solid was filtered off (wet wt. 10 gm., dry wt. estimated as 7.25 gm. or 0.05 mole) and immediately suspended in 50 cc. of acetic acid. To this was added 5.1 gm. (0.05 mole) of acetic anhydride. To this suspension at 10° to 15° C. was added over 30 min. a solution of 6.5 gm. (0.05 mole) of dibutylamine in 20 cc. of acetic acid. The solution was then heated to 40° C. No heat of reaction was observed and no nitrogen oxides were apparent. When the mixture was poured into ice and extracted with ether no trace of water insoluble material boiling above 80° C. could be found.

Negative results also were obtained when perchloric acid replaced hydrogen chloride in the attempted nitration of dibutylamine with nitric acid and acetic anhydride.

### Diisobutylamine

Diisobutylammonium nitrate was prepared by vacuum evaporation at 10 mm. of a solution made by neutralization of a diisobutylamine suspension with 70% nitric acid to brilliant yellow neutrality. The salt melted at 210° C., and several crystallizations from benzene did not raise this melting point.

When 28.8 gm. (0.15 mole) of diisobutylammonium nitrate, 16.3 gm. (0.16 mole) of acetic anhydride, 0.78 gm. (0.006 mole) of zinc chloride, and 0.20 cc. (0.0047 mole) of 100% nitric acid were mixed at 20° C. and allowed to stand for four hours the mixture became homogeneous and the temperature rose spontaneously to 40° C. When this solution was poured into 100 gm. of ice-water a yellow solid sank to the bottom while an oil separated on the surface. The oil and water were decanted from the solid and extracted five

\* This material always contained combined chlorine and melted at -35° to -25° C. The halogen-containing impurity was destroyed by boiling for 35 min. under reflux with five volumes of 70% nitric acid. After cooling, the whole was diluted with water, neutralized with alkali, and the oil taken up in ether, dried with magnesium sulphate and distilled. The distillate (80% recovery) boiled at 128° to 129° C. (11 mm.);  $n_D^{20}$  1.4545. It melted at -22° to -21.5° C. and gave a negative Beilstein halogen test.

times with a total of 100 cc. of ether. This ether solution was shaken with saturated aqueous sodium carbonate until blue to bromcresol green, then dried over sodium sulphate. Subsequent distillation, finally at 102° to 110° C. (11 mm.), gave 4.5 gm. of distillate which gave a strong Franchimont nitramine test. This 17% yield was redistilled at 104° C. (11 mm.). Calc. for  $C_8H_{18}N_2O_2$ : C, 55.2; H, 10.3; N, 16.1%. Found: C, 55.2; H, 10.3; N, 16.2%.

The solid which was precipitated on dilution of the reaction mixture was filtered off, washed with water and dried to weigh 8 gm. and melted at 51° to 62° C. This 33% yield was twice crystallized from ethanol to melt at 73.4° to 74.5° C., the melting point of diisobutylacetamide (12, 13).

#### *Dicyclohexylnitramine*

To a solution of 13.7 cc. (0.315 mole) of 99% nitric acid and 35.7 cc. (0.35 mole) of 92% acetic anhydride in 16 cc. (0.28 mole) of acetic acid, was added 15.24 gm. (0.07 mole) of dicyclohexylammonium chloride at 3° to 5° C. over 15 min. The resulting slurry disappeared on stirring for 25 min. at 25° C. One drop of the reaction mixture was added to 1 cc. of aqueous sulphamic acid and to this, after a few minutes, a crystal of potassium iodide. The characteristic dark brown color of iodine indicated the presence of much hypochlorous acid.

After five hours of stirring at 25° C., one-third of the reaction mixture was drowned in water. The crude nitramine weighed 9.35 gm., m.p. 116° to 123° C. This product (designated *A*) was separated chromatographically into a 48% yield of dicyclohexylnitramine (1 : 1 mole basis). The remainder of the product seemed to be dicyclohexylnitrosamine for the most part. The reaction mixture at this stage contained a small amount of electropositive chlorine.

After 22 hr. at 25° C. a second aliquot, one-third of the reaction mixture, was drowned in water. The weight of very crude nitramine, m.p. 99° to 119° C. (designated *B*), was 10.2 gm. (64% of theory). Separation as above yielded 50% of the theory of purified nitramine. The remainder was mostly nitrosamine since no dicyclohexylacetamide was found. A small test portion of the reaction mixture indicated a very slight amount of electropositive chlorine.

The remaining third of the reaction mixture was warmed to 40° C. for 90 min., cooled, the excess acetic anhydride hydrolyzed with 5.4 cc. (0.3 mole) of water, and the acids removed by distillation at 12 mm. The residual oil was drowned in 100 cc. of water and the precipitate filtered and washed; weight was 12.40 gm. This was processed by washing with two 60 cc. portions of warm ether. Weight of ether insoluble amine nitrate was 0.84 gm. (5% recovery). The ether washings on evaporation to dryness gave 10.93 gm. (*C*) of very crude dicyclohexylnitramine, m.p. 93° to 119° C. (50% of theory on the basis of thermal analysis), which was easily crystallized



from either warm 60° to 70° C. petroleum ether or warm aqueous ethanol to give a 45 to 50% yield of purified nitramine. It crystallizes in small white flakes, m.p. 134° to 134.5° C.

The nitramine is insoluble in water, dilute acids and alkali but very soluble in most organic solvents. It gives a positive Franchimont nitramine test.

The nitramine was decomposed by boiling for two hours with a solution containing 1 : 1 parts by weight of acetic acid : 70% aqueous sulphuric acid. It gave only 69% of the theoretical amount of nitrous oxide (1 : 1 mole basis). Calc. for  $C_{12}H_{22}N_2O_2$ : C, 63.7, H, 9.81; N, 12.4%. Found: C, 63.8; H, 9.80; N, 12.6%.

#### *Chromatography of the Crude Dicyclohexylnitramines*

Both dicyclohexylnitramine and dicyclohexylnitrosamine are very weakly adsorbed on either a 2 : 1 or 4 : 1 parts by weight adsorbent column of Merck's silicic acid : Johns-Manville Hyflo grade Celite. Complete separation of the nitrosamine and nitramine zones in a column 20 × 180 mm. was not effected when freshly distilled 60° to 70° C. Viking brand petroleum ether was employed as the developer. Dicyclohexylacetamide was easily separated, however, its zone being located near the top of the column. The separation in this column of the fractions designated as A, B, C in the experiment outlined above is indicated in Table II. The relative amounts of nitrosamine and nitramine in these fractions could be evaluated by thermal analysis according to the melting point composition diagram outlined in Fig. 1.

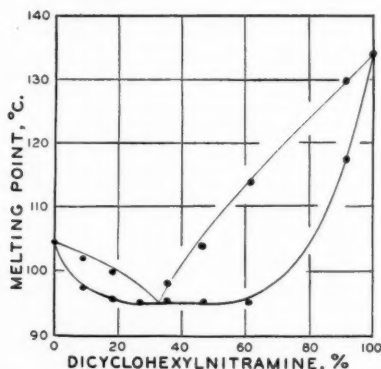


FIG. 1. Melting point diagram for the system dicyclohexylnitramine-dicyclohexylnitrosamine.

A 10% solution of diphenylamine in 95% sulphuric acid was found to be a satisfactory streaking reagent for locating the nitramine zone. It imparted a deep blue color. Since, however, no suitable streaking reagent was found for dicyclohexylacetamide, its location on the column was established by a synthetic mixture of known amounts of dicyclohexylnitramine, nitrosamine, and acetamide. It was assumed that under similar developing conditions, the position of the acetamide, if any were present in the crude nitramines, would be

identical with that found on the known sample. Thus the adsorbent was extruded from the column, the position of the nitramine determined by streaking with diphenylamine in concentrated sulphuric acid, and the position of the acetamide determined by measuring down the required distance from the top of the column.

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CATALYZED NITRATION OF AMINES<sup>1</sup>IV. THE ROLE OF ELECTROPOSITIVE CHLORINE IN THE NITRATION OF LYSIDINE<sup>1</sup>BY J. C. MACKENZIE, G. S. MYERS<sup>2</sup>, G. N. R. SMART<sup>3</sup>, AND  
GEORGE F WRIGHT

## Abstract

The nitration of lysidine with acetic anhydride, nitric acid, and a chloride catalyst does not yield the expected nitrolysidine. The product, instead, is 1,3-dinitroimidazolidone-2 when little or no chloride is used. A new compound is produced when a full equivalent of hydrogen chloride is included. This new compound is thought to be 1,3-dinitro-2-chloromethyl-2-acetoxylimidazolidine. Its decomposition products are ethylenedinitramine and chloroacetic acid. It is believed to be cyclic because the linear isomer, N-acetyl-N'-chloroacetyl ethylenedinitramine has been prepared and found not to be identical. The formation of dinitrochloromethylacetoxylimidazolidine in the nitration mixture suggests that it is formed by addition of chlorine acetate. This compound has been prepared, characterized, and found to add to allylbenzene. Since it will convert dicyclohexylamine to the chloramine it is postulated as a temporal ingredient of the catalyzed nitration mixture.

In connection with the study of catalyzed nitration of secondary amines, (5, 6, 7), the cyclic amine, lysidine, I, was chosen because of its apparent amidine structure. The proton-attracting power of this amine had previously been determined (7) as slightly less than that of dibutylamine. One might therefore expect that it would nitrate, if a few mole per cent of zinc chloride were added to the nitric acid and acetic anhydride, to give 1-nitrolysidine, II.

When the nitration was carried out under these conditions there was no indication that nitrolysidine was formed, but a low yield (7%) of the known 1,3-dinitroimidazolidone-2, V, was produced instead. Indeed this compound was produced in 20% yield when lysidine was added to nitric acid and acetic anhydride without any chloride catalyst. This result was not entirely incongruous. Mr. R. S. Stuart in this laboratory had once obtained the same compound by mixed acid nitration of thioimidazolidone-2 (VI→V). Likewise, in another research, when 2-nitramino- $\Delta^2$ -imidazoline was treated with large excesses of nitric acid and acetic anhydride, the only isolable product was V (11). In order to explain how lysidine might be nitrated to V, one might postulate its isomerization to III by 1,3-hydrogen shift. Some evidence for this isomerization has been obtained by ozonolysis in acetic acid to produce a 3% yield of formaldehyde (12). The nitration of III ought to give IV without chloride catalyst, since the vinylamino linkage is weakly basic. Subsequent oxidation of IV would lead to 1,3-dinitroimidazolidone, V.

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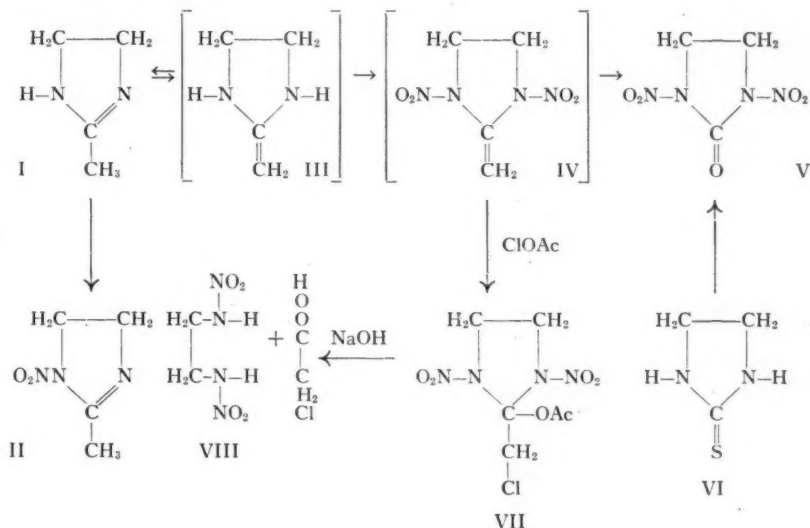
Contribution from the Chemical Laboratory, University of Toronto, Toronto, Ont.

<sup>2</sup> National Research Council Fellow 1944-45.

<sup>3</sup> Post-doctoral Fellow, University of Toronto, with grant-in-aid from the National Research Council, Ottawa, Canada.

EDITOR'S NOTE:—The subject of this paper has been released from security restrictions.

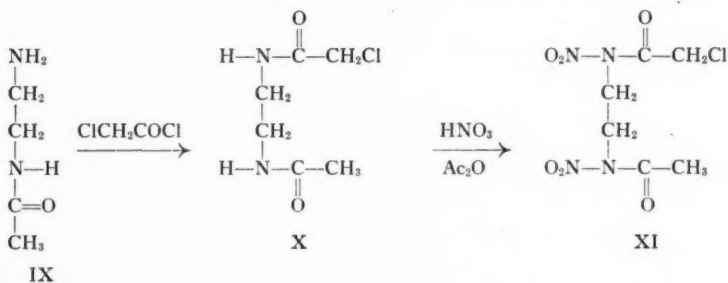
Since dinitroimidazolidone, V, was not the expected product, and was in any case obtained in low yield, we turned to the expedient of adding an equivalent of chloride as amine hydrochloride (5) and of using large excesses of nitric acid and acetic anhydride. Under these circumstances a new compound was obtained, in 30% yield if it were  $C_6H_9N_4O_6Cl$ . Its complete elemental analysis agreed with this formula. Furthermore, on alkaline hydrolysis it yielded 97% of the ethylenedinitramine, VIII, which might be expected from a compound having a structure in which the ethylenediamine portion of lysidine was present.



These facts suggested the cyclic structure 1,3-dinitro-2-chloromethyl-2-acetoxylimidazolidine, VII, but it was evident that a linear structure, N-acetyl-N'-chloroacetyleneethylenedinitramine could equally well explain these data. The latter compound was, however, synthesized from the known 2-aminoethylacetamide, IX (9), by chloroacetylation to X and subsequent nitration to N-acetyl-N'-chloroacetyleneethylenedinitramine, XI. This compound was not identical with the isomer that was obtained by the nitration of lysidine hydrochloride.

During the latter nitration a behavior was exhibited which we believe to be typical of acylnitramines. When a moderate excess of nitric acid and acetic anhydride (no catalyst is necessary) was employed, the product XI precipitated from the reaction mixture. On the other hand, when a large excess of acetic anhydride and nitric acid was used, no precipitation occurred, and none of the product XI could be isolated. This indicates that an acylnitramine is unstable in the nitrating mixture and will not be isolable unless it precipitates out of this environment.

It has previously been noted in the study of dibutylamine nitration (5) that some decomposition of the secondary amine occurs to give the corresponding primary amine. This might be expected to acetylate in the anhydride medium. Subsequent nitration of the resulting acylamine,



$\text{RNHCOCH}_3$ , might then introduce an unstable impurity into the main product, dialkylnitramine. The behavior of X in excess nitrating medium does however indicate that the acylnitramine will be decomposed, since it will be in low concentration, and hence remain in solution after nitration. In point of fact acylnitramines have never been detected as impurities in dialkyl-nitramines.

Since N-acetyl-N'-chloroacetylenehydrazine was not identical with the reaction product from the nitration of lysidine hydrochloride, we have postulated the alternative cyclic structure, VII. Although we have been unable to synthesize the substance having this structure by an alternate path, certain of its properties indicate that this is its structure. Thus its halogen atom is firmly bound, as might be expected of a primary chloride, and it would not react with hot alcoholic silver nitrate or silver acetate in boiling acetone or dioxane. Furthermore when the compound was hydrolyzed by alkali a good yield of chloroacetic acid (identified as 2,4-dichlorophenoxyacetic acid) was obtained. When the compound represented as VII was boiled with alcohol the acetoxy group (which had been detected by Feigl's lanthanum nitrate test) was replaced by the alkoxy group. This reaction is typical of the tertiary ester type of which VII is representative. The resulting methoxyl, ethoxyl, and *n*-propoxyl derivatives, unlike the parent acetoxy compound, are relatively stable toward alkali.

Evidence supporting the cyclic structure, VII, for the nitration product of lysidine hydrochloride, and also for its derivatives, the methyl, ethyl, and propyl ethers, is found by examination of the absorption spectra of these compounds. Thus it may be seen from Table I that the linear compounds ethylenedinitramine and N-acetyl-N'-chloroacetylenehydrazine tend to absorb at shorter wave lengths than the 2-acetoxy-, 2-methoxy-, 2-ethoxy-, and 2-propoxy-1,3-dinitro-2-chloromethylimidazolidine. In this sense they resemble the known 1,3-dinitroimidazolidone-2.

TABLE I  
ABSORPTION SPECTRA IN THE REGION 2300 TO 2500 Å IN ABSOLUTE ETHANOL

Compound	Absorption $\lambda$ , Å	Maximum, $E_{\max}$
Ethylenedinitramine	2320	12,850
N-acetyl-N'-chloroacetylenedinitramine	2350	11,360
1,3-dinitro-2-chloromethyl-2-acetoxylimidazolidine	2370	10,560
1,3-dinitro-2-chloromethyl-2-methoxylimidazolidine	2375	11,560
1,3-dinitro-2-chloromethyl-2-ethoxylimidazolidine	2380	10,360
1,3-dinitro-2-chloromethyl-2-propoxylimidazolidine	2380	11,090
1,3-dinitroimidazolidone-2	2420	10,030

If the structure VII is authentic, then its formation can best be explained by considering that chlorine acetate has been added to the double bond in the ephemeral intermediate, IV. It has been found previously (3) that chlorine acetate will add easily to allyl chloride or to cyclohexene. Alternatively this addition might have involved chlorine monoxide with subsequent ester interchange of an acetoxy group for a hypochlorite group, but discussion will be limited to the chlorine acetate concept, principally because it is convenient to consider the directed addition as electropositive chlorine to the terminal negative carbon atom and negative acetoxy to the more positive carbon that is involved in the ring.

The speculation that chlorine acetate might exist in the chloride-catalyzed nitration was warranted by a number of confirming tests for positive chlorine on aliquots of reaction mixtures that had been diluted into sulphamic acid (to remove nitrous acid). The possibility was further strengthened when it was found that chlorine (5) (chlorine chloride, in this sense) was a nitration catalyst.

In order to eliminate the effect of inorganic salts which would be present when chlorine acetate was prepared from chlorine and silver acetate, we prepared this reagent according to the method of Schützenberger (13) by adding chlorine monoxide to acetic anhydride. This solution cannot be distilled without explosion and, indeed, is very likely to explode without warning; it is not surprising that its chemistry is ill-defined. Indeed, Aronheim (2) has stated that Schützenberger's solution was not chlorine acetate at all, but only chlorine monoxide in acetic anhydride. It was therefore necessary for us to reinvestigate the chlorine monoxide - acetic anhydride system. This investigation revealed that some unknown factor, probably a catalyst, varied the rate of conversion of chlorine monoxide in acetic anhydride to chlorine acetate. There was considerable variation from lot to lot of the chlorine monoxide that we used. However, some conversion did finally occur at 0°C. and it could usually be accelerated by heating to 30° or 35° C., although much chlorine monoxide was lost during this heating process. The resulting solution still contained chlorine monoxide, which imparts a color to the solution. This

could, however, be removed by evacuation at  $0^{\circ}\text{C}$ . The record of this evacuation is shown in Fig. 1, where the iodometric titration value is plotted against time of evacuation. The discontinuity in the curve represents a con-

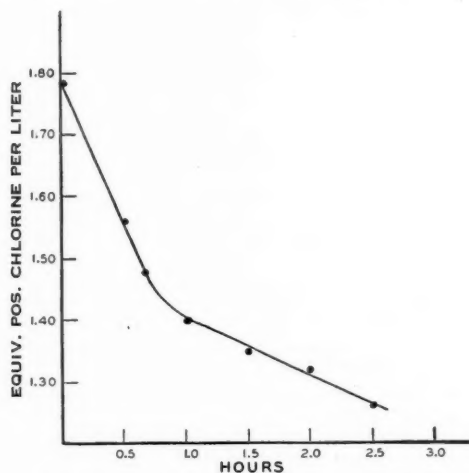


FIG. 1. Evacuation of chlorine monoxide-chlorine acetate-acetic anhydride system.

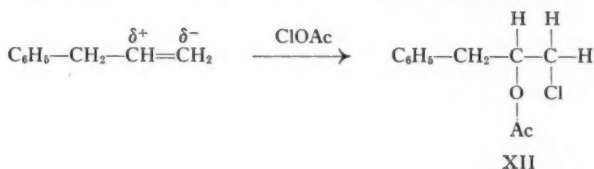
centration of positive chlorine (1.4 moles per liter) at which the solution is colorless, whereas solutions of chlorine monoxide at this concentration are strongly yellow. It would appear therefore that the rapid loss at the beginning of the vacuum evaporation is indeed chlorine monoxide, and this loss was observed by Aronheim on a solution which had not reacted to form chlorine acetate. Schützenberger's solution, like most of our own, contained both chlorine monoxide and acetate from which the former could be removed owing to its greater volatility. The question as to why Aronheim's solution, like a few of ours, failed to react when heated is at present not answered.

It sufficed for our purpose to have at hand a chlorine acetate solution in acetic anhydride so that its reactivity could be tested with respect to carbon-carbon unsaturation. There are only a few vicinal 1-acetoxy-2-chloro compounds recorded in the literature. We chose 2-acetoxy-3-chloro-1-phenylpropane, XII, from among these since chlorine acetate ought to add smoothly to allylbenzene to give this compound.

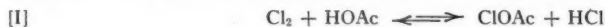
When allylbenzene was treated with the chlorine acetate solution the positive chlorine was taken up and only one compound was obtained whose properties agreed reasonably well with those previously reported (8). The elemental analyses and molecular refractions agreed with those calculated for XII. Oxidation in nitric acid and in chromic acid yielded *p*-nitrobenzoic and benzoic acid, respectively, as well as chloroacetic acid.



In order to demonstrate that a solution of chlorine in acetic anhydride would not behave in the same manner, allylbenzene was treated with such a solution under reaction conditions otherwise identical. A 62% yield of 2,3-dichloro-1-phenylpropane was produced. If any 2-acetoxy-3-chloro-1-phenylpropane was present, it was less than 5% of the theoretical yield.



Both products were obtained when allylbenzene was treated with a chlorine-acetic anhydride solution which had been diluted with acetic acid. The 2,3-dichloro-1-phenylpropane predominated as a 32% yield, but a 17% yield of 2-acetoxy-3-chloro-1-phenylpropane was obtained as well. These results indicate that the equilibrium postulated by Bockemüller and Hoffmann (Equation [I]) for chlorine does indeed exist in acetic acid. On the other hand, chlorine must remain as the element in acetic anhydride alone.



On the basis of addition to allylchloride (3) and to allylbenzene, chlorine acetate if present in the nitration mixture might be expected to add to 2-methyleneimidazolidine, III. The addition product, after subsequent nitration, would become dinitrochloromethylacetoxylimidazolidine, VII. The addition to III would, however, withdraw electropositive chlorine from the reaction mixture, since the reaction seems to be nonreversible (dinitrochloromethylacetoxylimidazolidine, VII, does not react with aqueous iodide). This withdrawal of chlorine acetate would effectively stop the nitration if only a catalytic quantity were present. An explanation is thus provided for the fact that lysidine, unlike dibutylamine which has comparable proton-attracting power, will not yield VII unless a large amount of chloride is present.

It would thus appear that chlorine acetate is present in the nitration mixture. In this event the secondary amine which is also present ought to react with it to form the corresponding chloramine if chloramination in acetic anhydride or acetic acid follows the normal course in aqueous solution (10). In order to test this possibility we treated dicyclohexylamine in acetic acid with a solution of chlorine acetate in acetic anhydride. We found that 40% of the added electropositive chlorine was converted to dicyclohexylchloramine, while 34% was reduced in some manner, since it was found as dicyclohexylammonium chloride.

This experiment demonstrates that if the original hydrogen chloride catalyst in the amine nitration were oxidized to electropositive chlorine, then some of this ought to be converted to the chloramine. Nevertheless a dialkylchloramine has never been detected among the nitration products, although

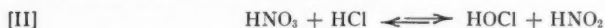
a special search was made in the case of dibutylamine nitration when the product was found to be contaminated with combined chlorine. One might surmise, therefore, that any chloramine which formed must further be altered by the other reagent in the nitrating mixture, namely nitric acid. The dialkylchloramine might thus be an intermediate in the nitration process.

Since chlorine acetate seemed to be the addend in the formation of dinitrochloromethylacetoxylimidazolidine, VII, the electropositive chlorine catalyst has been discussed in terms of this compound, but other chlorine esters would probably also be effective. Chlorine itself (as chlorine chloride) might be considered in this category, but actually there is doubt that it can act directly as the catalyst if catalyst activity is due to dialkylchloramine formation. Thus a solution of chlorine in acetic anhydride when treated with dicyclohexylamine gave a quantitative yield of dicyclohexylammonium chloride, but no dicyclohexylchloramine could be found.

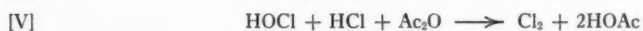
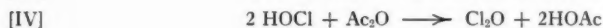
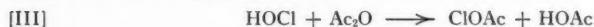
If the chloramine is intermediate in the nitration of strongly proton-attracting secondary amines then elemental chlorine, when it is used as a catalyst, evidently must act via the equilibrium outlined in Equation [I] between chlorine and acetic acid. In this connection it should be recalled (5) that addition of acetic acid to the nitrating mixture always enhances the yield of nitramine. According to Equation [I] this ought to increase the concentration of chlorine acetate.

The behavior of chlorine acetate in acetic anhydride would justify its consideration as an active species of the chloride catalyst. Thus it has been found to deteriorate spontaneously (3), somewhat faster at 20° C. than at 0° C., and this decomposition is accelerated by the presence of nitric acid, especially in excess. It is more stable in presence of zinc salts than in their absence. Dilution with acetic acid also stabilizes it. All these properties conform to the behavior of the catalyst in the nitration of dibutylamine (5). Of course, other types of positive chlorine compounds, such as chlorine monoxide or chlorine nitrate ought to behave in the same manner, so chlorine acetate should be considered only as representative of a class of active catalysts. If such chlorine esters are indeed the active catalysts, then their utilization would be most efficient in a medium containing much acetic acid, little nitric acid, and sufficient amine with which to capture them before they decompose spontaneously.

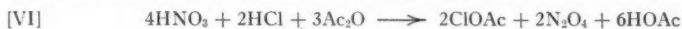
The formation of chlorine acetate in the catalyzed nitration mixture may be postulated as a variation of the familiar aqua regia reaction. If we consider the first stage of this reaction to be:



we may then expect the hypochlorous acid either to decompose or to be stabilized by acetic anhydride.



If Equation [III] represents the stabilization mechanism then the overall catalyst reaction may be written as Equation [VI].



Such a reaction scheme would explain the initial formation of nitrosamine in the nitration process, if the nitroso compound were to be formed from the free amine and nitrous acid (or its mixed anhydride).

### Experimental\*

#### Lysidine (4)

A mixture of 30 gm. (0.208 mole) diacetylenediamine (1) and 5 gm. (0.202 mole) of powdered magnesium was heated in a distillation flask at a temperature of 290° to 295° C. for 40 min. The lysidine distilled at 195° to 198° C. in the evolved hydrogen stream to yield 23.3 gm. melting at 65° to 82° C. and contaminated with ethylenediamine. This distillate was dissolved in 50 cc. of absolute ethanol. This solution was concentrated to yield 11.9 gm. of lysidine melting at 103.5° to 105° C. This 68% yield could further be purified with 80% recovery by distillation at 118° (30 mm.) to melt at 105° to 106° C.

If the ethanol solution was saturated with hydrogen chloride and evaporated to a small volume under reduced pressure, lysidine hydrochloride could be obtained by crystallization from hot absolute ethanol (0.9 cc. per gm.) in which ethylenediamine dihydrochloride is insoluble. The first crop was augmented by dilution of the filtrate with acetone to give a total yield of the hydrochloride which was 37% of theoretical. It melted at 163° to 167° C.

#### 1,3-Dinitro-2-chloromethyl-2-acetoxylimidazolidine, VII

To 557 gm. (5.45 moles) of acetic anhydride at -50° C. was carefully added over 20 min., 301 gm. (4.79 moles) of nitric acid as 207 cc. of 98% concentration. Then 82 gm. (0.68 mole) of lysidine hydrochloride was added quickly (over five minutes). The slurry was stirred at -50° C. for 15 min., at which time an aliquot diluted into water gave no water insoluble product. The slurry was then warmed gradually over a 20 min. period. Solution occurred at -40° to -35° C. As the temperature rose from -2° to 0° C. brown fumes became apparent. After 30 min. at 0° to 4° C. an aliquot into water gave an insoluble product, m.p. 150° to 154° C. Fifteen minutes later (temp. 7° C.) a precipitate appeared in the reaction mixture. The temperature was allowed to rise to 20° C. over 20 more minutes, maintained for 15 min., then lowered to 0° C. The slurry was subsequently poured on ice and water for a final dilution to 1500 cc. When hydrolysis was complete, the precipitate was filtered off and washed free from acid. The yield of the very crude material was 87 gm., m.p. 140° to 144° C. or 48% of theoretical. Further dilution of the filtrate gave an oil resembling chloropicrin in odor. The crude product, when crystallized from ethyl acetate (4 cc. per gm.), gave a 75% recovery of material, m.p. 164° to 164.5° C. An alternative purification involved dilution

\* All melting points have been corrected against reliable standards.

of an acetone solution (4 cc. per gm.) with an equal volume of water. The impurity which was removed by these crystallizations was proved to be ethylenedinitramine.

An alternate method of preparation involving 1 mole lysidine : 7.3 moles nitric acid : 8.2 moles acetic anhydride : 1.3 moles acetyl chloride under essentially the same reaction conditions gave a lower yield; 36% of crude material or 26% of the pure product. Calc. for  $C_6H_9N_4O_6Cl$ : C, 26.8; H, 3.38; N, 20.8; Cl, 13.2%. Found: C, 26.9; H, 3.52; N, 20.9; Cl, 13.0%.

The compound gives a positive Franchimont test and, after decomposition with concentrated sulphuric acid, a positive test for acetic acid can be obtained with lanthanum nitrate (Feigl). A negative test for chloramine was obtained with aqueous potassium iodide and the halogen was indeed tightly bound, since no precipitation occurred when the compound was boiled with alcoholic silver nitrate.

#### *Alkaline Hydrolysis of VII*

One gram of this substance was hydrolyzed by 20 minutes' reflux with 12 cc. of 5% aqueous sodium hydroxide. Acidification with 4 cc. of concentrated hydrochloric acid (pH 1) followed by filtration and then extraction of the vacuum-evaporated filtrate with acetone gave a total of 0.54 gm. of ethylenedinitramine, m.p. 177° C., which was 97% of that expected on the basis of the proposed structure. Decomposition of this substance, VII, to ethylenedinitramine is extremely easy. It occurs on solution in pyridine, or spontaneously over a period of months at room temperature. Furthermore, the compound is destroyed rapidly in 2 *N* alkali at 25° C.; about five equivalents were consumed. When the imidazoline was treated carefully with minimal amounts of alkali no product intermediate between the original material and ethylenedinitramine could be isolated.

Chloroacetic acid was identified among the alkaline decomposition products by stirring a solution of 1.00 gm. (0.00373 mole) of VII in 10 cc. of dioxane at 4° C. with a solution of 0.6 gm. (0.0149 mole) of sodium hydroxide in 3 cc. water. After eight hours the pH of the medium was about 8. The dioxane was then evaporated off under reduced pressure.

To the residue was then added 0.6 gm. (0.00373 mole) of 2,4-dichlorophenol and 0.18 gm. (0.0045 mole) of sodium hydroxide in 1.8 cc. of water. The mixture was heated quickly to 65° C. and then to 97° C. over 50 min., while crystals formed. After an additional heating period of 75 min. at 98° C., the whole was diluted with 8 cc. of water and acidified with 0.6 cc. of concentrated hydrochloric acid. The organic components were taken up in ether, washed four times with a total of 100 cc. water, dried with sodium sulphate, and the ether evaporated. The residue was extracted four times with 4 cc. portions of boiling benzene, in which ethylenedinitramine is insoluble. The combined benzene extracts were washed with saturated sodium bicarbonate. Acidification of the aqueous phase yielded 0.58 gm. of 2,4-dichlorophenoxyacetic acid, m.p. 134° to 135° C., which was crystallized from

benzene (3 cc. per gm.) to melt at 139° to 140°C. The yield of chloroacetic acid must therefore be at least 72% of theoretical.

An attempted oxidation of dinitrochloromethylacetoxylimidazolidine, VII, with chromic anhydride in acetic anhydride at 25° to 30° C. over eight days yielded only 55% of the original material. The loss can be explained by the instability of the decomposition product, ethylenedinitramine, in this medium. While VII seemed to give one equivalent of gas in the Zerewitinoff apparatus with methylmagnesium iodide this result is of doubtful significance, since it has been found in this laboratory that 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) likewise gives gas in this analysis.

*1,3-Dinitro-2-chloromethyl-2-alkoxyimidazolidine*

When dinitrochloromethylacetoxylimidazolidine was boiled with alcohols it dissolved after a time. On cooling to 0° C. the corresponding alkoxy derivative precipitated in an impure form which was subsequently purified by crystallization.

Moles alcohol per mole imidazolidine	React. time, hr.	Cryst. medium	Yld., %	M.p., ° C.	Analyses					
					Calc.			Found		
					C	H	N	C	H	N
74 CH <sub>3</sub> OH	6.5	Acetone 1, Water 1	75	157.5 to 158	24.9	3.77	23.3	25.2	4.07	23.0
52 C <sub>2</sub> H <sub>5</sub> OH	7.5	Pet. ether b.p. 60° to 70° C.	83	130 to 130.5	28.3	4.35	22.0	28.4	4.42	22.5
40 <i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	9	Pet. ether b.p. 60° to 70° C.	69	93.4 to 93.8	31.3	4.88	20.8	31.1	4.84	20.8

In each case further product could be obtained by evaporation of the alcohol solution, but it was badly contaminated with ethylenedinitramine and starting material.

When 1,3-dinitro-2-chloromethyl-2-ethoxyimidazolidine was boiled in dioxane with 2.5 equivalents of sodium acetate over 50 hr. the compound was largely recovered unchanged. It was recovered (52%) after attempted oxidation with chromic anhydride in acetic anhydride. In a comparable attempted oxidation of dinitroimidazolidone, 90% was recovered unchanged.

*1,3-Dinitroimidazolidone-2*

To a solution of 0.03 gm. (0.00048 mole) of nitric acid (5% of total) in 1.53 gm. (0.0150 mole) of acetic anhydride at 15° C. were added proportionately over 17 min. 0.25 gm. (0.0030 mole) of lysidine and 0.82 gm. (0.013 mole) of 99% nitric acid. The yellow solution, which evolved brown fumes slightly, was stirred at 5° C. for five hours. No solid product was formed at this time, even after heating to 56° C. A repetition of the experiment showed that the reaction mixture at 5° C. began to precipitate a solid after six and one-half

hours and this was augmented after 10 hr. longer at the same temperature. However, this precipitate did not reach its maximum until 15 hr. more (at 25° C.) had elapsed. The reaction mixture was then evaporated under reduced pressure and the residue extracted with ether. Evaporation of this ether yielded 0.16 gm. of crude dinitroimidazolidone, or 21% of theoretical. This was crystallized from water-acetone to melt at 216° to 216.5° C. A mixed melting point with true dinitroimidazolidone was not lowered.

Alternatively a solution of 0.12 gm. (0.0009 mole) of zinc chloride, 0.45 cc. (0.01 mole) of 99% nitric acid, and 30 cc. (0.3 mole) of acetic anhydride was prepared at 5° C. and stirred while 5.04 gm. (0.06 mole) of lysidine and 10.87 cc. (0.26 mole) of nitric acid were added proportionately at 15° C. over 30 min. After five hours at 6° C. a white precipitate began to form. The reaction mixture was stirred for eight hours longer at 6° C. and then filtered to yield 0.5 gm. (7% of theory) of dinitroimidazolidone, m.p. 213° C. After crystallization from ethanol, toluene, and nitromethane, this melted at 216° to 217° C.

This compound was not obtained when 1 mole of 1,3-dinitro-2-chloromethyl-2-acetoxyimidazolidine, VII, was treated with 21 moles of 99% nitric acid in 28 moles of acetic anhydride at 40° C. either with or without 0.03 mole of zinc chloride. Instead 92 to 98% of the dinitro compound, VII, was recovered unchanged.

*N-Acetyl-N'-chloroacetylenediamine*

To a solution of 6.77 gm. (0.0657 mole) of 2-aminoethylacetamide (9) in 20 cc. water at 5° to 10° C. was added 2.78 gm. (0.0695 mole) of sodium hydroxide as a 10% aqueous solution. To this solution at -3° C. was added dropwise with stirring 7.84 gm. (0.0695 mole) of chloroacetyl chloride (b.p. 100° to 115° C.) over 30 min. The resulting solution (pH 3) was continuously extracted with chloroform to yield 9.12 gm. or a 78% molar yield melting at 143° to 144° C. This was crystallized from acetone-ethanol (5 : 1) to melt at 146.5° to 147.0° C. Calc. for  $C_6H_{11}N_2O_2Cl$ : C, 40.3; H, 6.21; N, 15.7%. Found: C, 40.4; H, 6.24; N, 15.7%.

*N-Acetyl-N'-chloroacetylenedinitramine*

To 3.88 gm. (0.0457 mole) of 99% nitric acid was added dropwise at 2° to 3° C. 2.07 gm. (0.0203 mole) of acetic anhydride. This solution was stirred and maintained at 2° to 3° C. over 10 min. while 0.89 gm. (0.005 mole) of N-acetyl-N'-chloroacetylenediamine was added. Although a white precipitate formed shortly after completion of addition, the mixture was maintained at 0° C. for six hours, then hydrolyzed during an hour with 14.4 gm. of ice. The water insoluble product was filtered off and washed acid-free with 80 cc. of cold water. The yield of the nitramine melting at 130° to 131° C. was 1.23 gm. or 95% of theoretical. After crystallization by solution in one part of acetone to which one part of cold water was added, this melted at 130.2° to 130.5° C. Calc. for  $C_6H_9O_6N_4Cl$ : C, 26.8; H, 3.38; N, 20.9%. Found: C, 27.0; H, 3.55; N, 21.1%.



When this nitration was repeated using a larger excess (169 gm., 1.65 moles) of acetic anhydride under otherwise identical conditions, no water insoluble product was obtained.

*Preparation and Identification of Chlorine Acetate*

Twice-distilled chlorine monoxide, 20 gm. (0.23 mole), was distilled into 23.4 gm. (0.212 mole) of acetic anhydride, in an all-glass apparatus in order to avoid explosion. The resulting red solution was unstable and frequently exploded when warmed from its storage temperature ( $-70^{\circ}\text{C}.$ ) to  $-20^{\circ}\text{C}.$  Aliquots were withdrawn for the following experiments.

A. This solution behaved as if it contained both chlorine monoxide and chlorine acetate. When 0.8206 gm. at  $10^{\circ}\text{C}.$  was placed under 10 mm. pressure for seven minutes it lost 0.3925 gm. The yellow liquid which remained, wt. 0.4281 gm., contained 0.00146 equivalents if it were chlorine acetate (thiosulphate titration), or 18% of the original electropositive chlorine.

B. When a second aliquot of the original solution (1.0985 gm.) was warmed to  $30^{\circ}$  to  $35^{\circ}\text{C}.$  for 15 min., the red color of chlorine monoxide disappeared. The remaining yellow solution weighed 0.8520 gm., which represents a loss of 51% of the electropositive chlorine. The difference between the iodometric titration of this yellow solution before and after being placed under a 10 mm. pumped vacuum for seven minutes indicated an equivalent weight of 43 for the material lost. Since the equivalent weight of chlorine acetate is 47 and that of chlorine monoxide is 21.8, the yellow solution probably still contained some chlorine monoxide.

C. A third aliquot of the original solution was repeatedly diluted with acetic anhydride while change in color and intensity was noted.

Mole $\text{Ac}_2\text{O}$ Mole $\text{Cl}_2\text{O}$	Equiv. electropositive chlorine per liter	Color
4	4.65	Red-brown
8	2.33	Light brown
12	1.55	Yellow, very faint red
16	1.16	Yellow
20	0.93	Pale yellow
24	0.78	Almost colorless

D. A fourth aliquot was diluted with acetic anhydride and let stand at  $0^{\circ}\text{C}.$  for six days until the red-brown color had faded to yellow. It was then placed under 12 mm. of pumped vacuum for half-hour periods, between which the residue was titrated. The tabulated data are plotted in Fig. 1.

A comparison of the concentration at the inflection in the curve, Fig. 1, with the concentration at which the samples in C and D became colorless indicates that a component less volatile than chlorine monoxide existed in this solution.



By contrast with the behavior of this solution, a chlorine solution of 10.3 mole % in acetic anhydride (saturated solution at 25° C.) lost 97% of the electropositive chlorine content after 150 min. evacuation at 0° C. under 12 mm.

Time, min.	Equiv. electro-positive chlorine per liter	Color
0	1.78	Yellow
30	1.56	Yellow
60	1.40	Colorless
90	1.35	Colorless
120	1.32	Colorless
150	1.26	Colorless

*E.* The decomposition of stoppered chlorine monoxide-chlorine acetate solutions in acetic anhydride was examined over a 24 hr. period under the following conditions:

—	Soln. at 0° C.	Soln. at 20° C.	Soln. at 0° C. with Zn(OAc) <sub>2</sub>	Soln. at 0° C. with ZnCl <sub>2</sub>	Soln. at 0° C. with HOAc	Soln. at 0° C. with 0.2 eq. HNO <sub>3</sub>	Soln. at 0° C. with 2 eq. HNO <sub>3</sub>
Initial Cl <sup>+</sup> /liter	0.1298	0.1242	0.1264	0.1292	0.1272	0.1271	0.1268
Final Cl <sup>+</sup> /liter	0.1163	0.0820	0.1212	0.1259	0.1227	0.1157	0.0906

This definite loss in positive chlorine only partially appears as chloride. Thus an initial concentration of Cl<sup>+</sup>, 0.00427 eq. per gm., and Cl<sup>-</sup>, 0.00044 eq. per gm., becomes Cl<sup>+</sup>, 0.00286 eq. per gm., and Cl<sup>-</sup>, 0.00109 eq. per gm. At least 70% of the missing 0.00076 eq. per gm. of chlorine can be discovered as chloride (Cl<sup>-</sup>) if the anhydride solution is heated with acetic acid and zinc dust before titration.

#### *Reaction of Chlorine Acetate with Allylbenzene*

Allylbenzene,  $n_D^{25}$  1.5105, b.p. 156° to 157° C., 3.54 gm. (0.03 mole) was treated over five minutes with 10.4 cc. of a solution of chlorine acetate (0.015 mole) in acetic anhydride at -15° C. The yellow solution was allowed to warm to room temperature overnight. The acetic anhydride was distilled off at 10 mm. and the oily residue washed with water, taken up in ether, and dried over magnesium sulphate. The ether extract gave 2.19 gm. of a yellow liquid, b.p. 133° to 143° C. (11 mm.), believed to be identical with the 2-acetoxy-3-chloro-1-phenylpropane prepared by Fourneau and Tiffeneau

(8) (68% crude yield). Redistillation gave a fraction, b.p. 134° to 136° C. (11 mm.);  $n_D^{25}$  1.5167;  $d_4^{25}$  1.14;  $MR_D^{25}$  56.4 (calculated 55.9), and a second fraction, b.p. 138° to 141° C. (11 mm.);  $n_D^{25}$  1.5153;  $d_4^{25}$  1.143;  $MR_D^{25}$  56.4 (L.L.).

The constants reported by Fourneau and Tiffeneau were b.p. 147° to 148° C. (15 mm.) and  $d$  1.16.

#### *Oxidation of 2-Acetoxy-3-chloro-1-phenylpropane*

Following the technique of Bockemüller and Hoffmann (3), 0.2 gm. ( $9.6 \times 10^{-4}$  mole) of a fraction boiling at 136° to 140° C. (11 mm.) obtained by addition of chlorine acetate to allylbenzene was boiled five hours in 10 cc. of methanol containing 0.25 cc. concentrated hydrochloric acid. The solvent was removed, finally under reduced pressure. The oily residue was treated with 0.5 cc. of 70% nitric acid and 0.2 cc. of 98% nitric acid. It was heated to 50° – 60° C. for three hours, then cooled and the nitric acid evaporated under reduced pressure. The semicrystallized residue was extracted with 0.3 cc. water and filtered to yield 0.04 gm. of yellow solid melting at 175° to 190° C. This was twice crystallized from water to melt at 237° to 238° C. A mixed melting point with *p*-nitrobenzoic acid was not lowered.

The 0.3 cc. aqueous washing liquor was treated with 0.05 gm. ( $3.1 \times 10^{-4}$  mole) of 2,4-dichlorophenol and 0.13 cc. of 30% aqueous sodium hydroxide. This was heated one hour at 100° C., then cooled and acidified with hydrochloric acid. The precipitated oil was taken up in ether. This ether solution was extracted with 2 cc. saturated aqueous sodium bicarbonate. This aqueous extract was acidified with hydrochloric acid to yield 0.01 gm., m.p. 124° to 125° C. Crystallization from 1 cc. petroleum ether (b.p. 60° to 70° C.) raised this melting point to 136° to 137° C. (micro). A mixed melting point (micro) with 2,4-dichlorophenoxyacetic acid was not depressed.

Oxidation of acetoxychlorophenylpropane was also effected by warming 0.1 gm. ( $4.7 \times 10^{-4}$  mole) of the compound to 70° to 80° C. in 4.9 cc. ( $3 \times 10^{-4}$  mole) of a potassium dichromate-sulphuric acid solution for 45 min. The cooled solution was extracted with ether. The ether solution was extracted with 5% aqueous sodium hydroxide. The remaining ether solution gave no qualitative tests for presence of a ketone. When the alkaline solution was acidified it yielded an oil which quickly solidified and melted at 67° to 104° C. It weighed 0.01 gm. At least 80% of it was benzoic acid according to the weight and melting point of 123° C. following crystallization from water. A mixed melting point was not lowered.

#### *Reaction of Chlorine in Acetic Anhydride with Allylbenzene*

At 0° C. a saturated solution of chlorine in acetic anhydride contains 2.39 moles chlorine per kilo of solution. To 0.1 mole chlorine in this chilled solution was added 11.8 gm. (0.1 mole) of allylbenzene over five minutes. The temperature rose to 30° C. After one hour at 0° C. to complete the reaction, the acetic anhydride was distilled off under 10 mm. The residue was distilled to give 9.37 gm. boiling at 115° to 137° C. (8 mm.),  $n_D^{25}$  1.5337,

as well as 3 gm. boiling below and above this range, with lower refractive index. If the principal fraction were 2,3-dichloro-1-phenylpropane, the yield would be 50% of theoretical. This material was redistilled to give a middle fraction, b.p. 121° to 123° C. (11 mm.);  $n_D^{25}$  1.5387;  $d_4^{20}$  1.192;  $MR_D$  calc. 50.1, found 49.7. This was redistilled at 115° C. (8 mm.). Calc. for  $C_9H_{10}Cl_2$ : Cl, 37.6%. Found: Cl, 37.0%. The final fraction distilled at 136° to 140° C. (11 mm.) and was probably impure 2-acetoxy-3-chloro-1-phenylpropane,  $n_D^{25}$  1.5267.

This experiment was repeated identically except that 50 gm. of acetic acid was included in the chlorine-acetic anhydride solution. The principal fraction (11.0 gm.) boiling at 117° to 137° C. (11 mm.) had a lower refractive index,  $n_D^{25}$  1.5272, than that obtained in acetic anhydride alone. On redistillation this gave 6 gm. boiling at 122° to 127° C. (11 mm.),  $n_D^{25}$  1.5351 (probably impure 2,3-dichloro-1-phenylpropane), and 3.5 gm. boiling at 136° to 140° C. (11 mm.),  $n_D^{25}$  1.5175,  $d_4^{25}$  1.152, which ought to be 2-acetoxy-3-chloro-1-phenylpropane,  $MR_D$  calc. 55.9, found 55.5. This was redistilled at 132° to 133° C. (8 mm.),  $n_D^{25}$  1.5179. Calc. for  $C_{11}H_{10}O_2Cl$ : Cl, 17.0%. Found: Cl, 17.5%.

#### *Dicyclohexylchloramine from Chlorine Acetate*

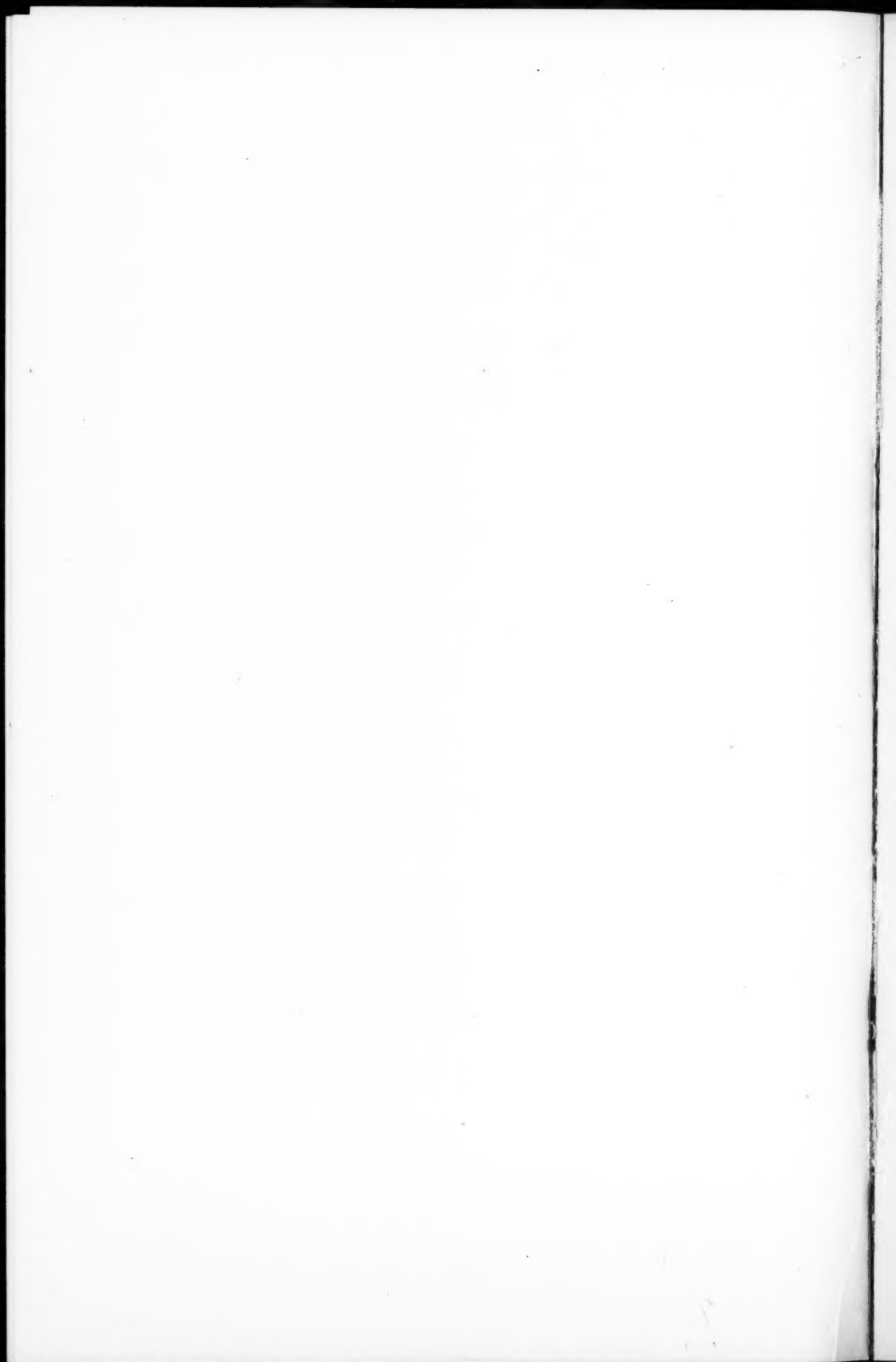
To a solution of 0.67 gm. (0.0037 mole) of dicyclohexylamine in 4 cc. of acetic acid was added 5 cc. of a solution of chlorine acetate in acetic anhydride (0.00254 mole) which was free from chlorine monoxide. The reaction mixture was digested 30 min. at 20° to 25° C. and then the unchanged chlorine acetate (6.5% of initial) and the acetic acid were distilled off at 10 mm. The acetic anhydride in the residue was hydrolyzed and the acetic acid removed at 10 mm. The residue was separated with ether into 0.22 gm. of dicyclohexylammonium chloride (34% on chlorine basis) and 0.16 gm. of dicyclohexylchloramine (40% on chlorine basis). The salt was identified by its melting point (320° to 332° C.) and by conversion to its picrate in 16% yield. The chloramine was identified by melting point (25° to 26° C.) and mixed melting point with a true specimen.

By contrast, a solution of 6.7 gm. (0.037 mole) of dicyclohexylamine in 40 cc. acetic acid was added below 20° C. to 2.17 gm. (0.0286 mole) of chlorine in 25 gm. of acetic anhydride (saturated solution at 0° C.). The solvent was subsequently removed under 10 mm. and the residue filtered in ethyl ether suspension to remove 6.2 gm. of dicyclohexylammonium chloride, identified by conversion and distillation of the amine. No cyclohexylamine or chlorinated amine was present. The yield was quantitative on the basis that one mole of chlorine gave one mole of hydrogen chloride.

Evaporation of the ethereal filtrate left 3.64 gm. of residue from which no dicyclohexylchloramine could be isolated by solution in ethanol and subsequent cooling to -70° C. This oil gave negative tests for presence of aldehydes or ketones.

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